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STUDY OF METHODS FOR IMPROVING
SYNTHETIC QUARTZ CRYSTALS

Report No. 8

(Continuation of Contract No. DA-36-039-SC-87372)

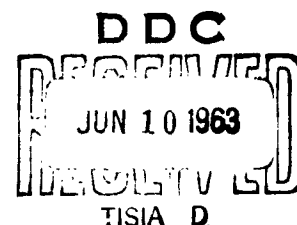
Contract No. DA-36-039-SC-89152

DA Project No. 3A99-15-001

Interim Final Report

1 January 1962 to 31 December 1962

U.S. Army Signal Research and Development
Laboratory, Fort Monmouth, New Jersey



Object: To grow quartz under ultrapure conditions, to study imperfections in the grown crystals and other selected crystals by optical and X-ray methods, to measure Q of precision resonators from selected crystals, and to correlate the parameters, leading to improvements in mechanical Q.

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STUDY OF METHODS FOR IMPROVING
THE QUALITY OF SYNTHETIC QUARTZ

INTERIM FINAL REPORT

1 January, 1962 to 31 December, 1962

1. PURPOSE

Based on Technical Guidelines of July 25, 1961, and Proposal of October 27, 1961, the efforts of this project are three-fold:

To bring imperfections in synthetic quartz into visual observation by means of monochromatic, parallel, plane polarized light, and by means of X-ray diffraction. To study quartz grown in this laboratory and by other organizations (Sawyer Research Products and Western Electric) as well as natural quartz. To examine the infrared absorption in the 3μ region in selected plates.

To have 5 Mc resonators (35AA-type) made from selected crystals, and to study the Q of these down to liquid nitrogen temperatures.

To grow quartz crystals large enough for resonator making with as high purity as possible in two 250-ml government-furnished platinum-lined autoclaves. Also, to grow quartz of high freedom from certain common impurities, especially aluminum, by using special nutrients in these and in the usual high-chrome steel vessels. To grow crystals under these conditions on specially selected Z-cut seed plates.

It is hoped that correlations and interpretations of the results may lead to methods for growing quartz of Q higher than hitherto possible.

2. ABSTRACT

The local strain fields surrounding internal defects in quartz plates were used to obtain their images by both polarized light and X-ray diffraction contrast. Dislocations were delineated with a resolution of the order of 20 microns, and their densities were found to range from zero up to 10^4 lines per cm^2 . No clear correlation could be found between dislocation content and the Q values measured between liquid nitrogen and room temperatures. Patterns of varying concentration of point defects were observed, particularly bands or "blankets" formed during the crystal growth process. Evidence suggests that, where such banding is present, the Q is significantly lowered. A theory is advanced that accounts for this by an interfacial acoustic scattering process.

The strain associated with banded growth was also observed to cause appreciable optic biaxiality.

The dislocations were observed to lie in directions approximately perpendicular to the growth surfaces, and to be essentially all edge dislocations arising from (a) pre-existing dislocations in the seed plate, (b) initiation of growth at the seed surface, (c) inclusions formed during growth, and (d) regions of intensely concentrated point defects. Some of the most significant observations were made by X-ray diffraction photography of precision resonators used for Q measurements.

Measurements of Q vs temperature were made on BQ61A-5 precision 5 Mc resonators made by Bliley Electric Company, over the range from liquid nitrogen to room temperature. Twelve runs were made on resonators from natural quartz, Clevite synthetic, Sawyer Research Products synthetic, and Western Electric synthetic. The latest group of resonator units from Bliley was He-filled, improving temperature measurement and control.

Loss peaks were observed at -110°C and -140°C for some of the resonators. These peaks have not been identified.

Regarding the growing of quartz under the Contract, emphasis was laid on high purity crystals since the presence of aluminum as an impurity has been often indicated as a probable cause of the lowering of Q, particularly at low temperature. Three nutrient materials of unusual purity (including high freedom from aluminum) were used: Corning #7940 "100% Silica," vitreous "Lump Silica" from L. Light & Company, and gel from distilled ethyl silicate. These were put through a stage of devitrification before they were used in the growth runs.

These materials yielded in general high purity quartz, but the visual quality was damaged by crevicing and cracking, except for the "Lump Silica." The nutrients exhibit a high rate of dissolution, believed to be a factor in the defective quality. A crystal grown from Corning silica was analyzed and was found to contain 0.89 ppm of Al, believed to be an all-time low figure for synthetic or natural quartz.

Two platinum-lined 250 ml vessels were used in this study. The seal is made by compression on the upper turned-out lip of the lining, the seal and dimensions being satisfactory for a working pressure of 15,000 psi.

Three growth runs were made using phosphorus as a pentavalent additive in the form of phosphate. Since phosphorus may enter the crystal substitutionally it may well act as an antidote for aluminum impurity thus avoiding interstitial compensating ions which may take part in this acoustical absorption. The crystals produced are of insufficient size for making 5 Mc resonators.

3. PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

D. R. Hale gave a talk on the history, growth process, and structure perfection of synthetic quartz before the Northern Ohio Geological Society, January 10.

A. E. Carlson, D. R. Hale, and Hans Jaffe attended the Sixteenth Annual Frequency Control Symposium, Atlantic City, April, 1962.

Mr. Joseph M. Stanley of the Signal Research & Development Laboratory visited Clevite on the 8th day of May, 1962, and on the 13th day of December, 1962, for discussions of problems and progress under the Contract.

On May 25, Dr. H. H. Pfenninger visited the Division and discussed the subject of his University of Zürich thesis, "Diffusion of Cations and Precipitation of Metals in Quartz by the Action of an Electric Field."

Dr. Fritz Laves, Director of the Institut für Kristallographie und Petrographie of the Eidg. Technische Hochschule, Zürich, visited on August 20, 1962, exhibiting electrolyzed quartz specimens and discussing fundamental problems relating to the defects in quartz.

Dr. Otto W. Flörke of the same Institut visited on August 23. He discussed the properties of Swiss quartz and talked over the growing procedures for quartz.

4. FACTUAL DATA

4.1 Introduction to Problem of High γ in Quartz

Investigation by Bömmel, et al.⁽¹⁾ demonstrated several relaxation acoustic loss mechanisms in quartz. These processes are identified as peaks in the curves of energy absorption vs frequency. Bömmel's 5 Mc-20°K peak was ascribed to motion of pinned dislocation segments, and was predicted to occur at room temperature at a frequency of 180 Mc. This prediction indicated that room temperature Q at 100-200 Mc would be severely affected by crystal imperfections. To study

¹⁾ Bömmel, H. E., Mason, W. P., and Warner, A. W., Jr.
Phys. Rev., 99, 1894-1896, 1955; 102, 64-71, 1956.

the effect of growth variables on high frequency losses, work was performed by this laboratory on Contract DA-36-039-SC-78247,⁽²⁾ ending November, 1959. Q at 100 to 200 Mc was found relatively insensitive to crystal quality, and no peaks of Q vs temperature were found that were deemed at that time to be markedly significant, except for rising loss at the lower end of the temperature range studied. This was interpreted as being the upper side of Boumel's 5 Mc - 50°K impurity relaxation peak.

It would seem reasonable to suppose that many other relaxation mechanisms may be possible in quartz; as many, indeed, as all the kinds and combinations of known impurities, vacancies, and dislocations in quartz. If a number of such were present, but each weak individually, they could account for much of the generalized, broad variations in Q that are observed. As a consequence, under the previous contract DA-36-039-SC-87372⁽³⁾, two approaches were followed in order to obtain information leading to ultimate reduction of the remaining, unknown, loss mechanisms:

- 1) Growing conditions were studied that would lead to crystals of highest purity.
- 2) Means were developed to bring dislocations, and if possible, other defects, under direct observation by means of polarized light and X-ray diffraction. The results were promising, and the work was continued and extended under the current contract. Selected crystals were chosen for fabrication into precision 5 Mc oscillators from which internal friction measurements could be made for correlation with growth and defect observations.

²⁾ Hale, D. R. and Krueger, H. H. A., "Study of Methods for Improving the Quality of Synthetic Quartz," Contract DA-36-039-SC-78247, Final Report, January 8, 1960.

³⁾ Hale, D. R. and Carlson, A. E. "Study of Methods for Improving Quality of Synthetic Quartz," Final Report, Contract DA-36-039-SC-87372, October 31, 1961.

4.2 Observation of Imperfections

4.2.1 Experimental Methods for Studying Imperfections

4.2.1.1 Optical Methods

It was shown by Bond and Andrus⁽⁴⁾ that the lattice strain around an edge dislocation in silicon is enough to cause useably detectable birefringence of transmitted polarized infrared light. The photographed patterns were about 50 microns across and had the predicted rosette configuration seen when an edge dislocation is viewed end-on. Indenbom and Tomilovskii⁽⁵⁾ gave the theory in more detail, and obtained similar dislocation strain rosettes with visible light in corundum (Al_2O_3) crystals. In the First Quarterly Technical Report of the previous contract⁽³⁾ we calculated that the dislocation strain birefringence in quartz should be about $1/3$ the intensity of that in silicon. It was felt that this should be usable, providing the background anisotropy and optical rotation in quartz could be nulled or "compensated."

The strong optical rotation of polarized light along the Z axis in quartz was a problem not faced by our predecessors. Furthermore, this rotation is strongly dispersed -- varying from 16° per millimeter for $\lambda = 7000 \text{ \AA}$ up to 51° per millimeter at 4000 \AA . Thus the light used, or at least that portion transmitted to a film or other sensor, must be as monochromatic as possible. Also, the specimen plates should thus have their opposing surfaces as flat and parallel as possible. Finally, the background anisotropy of quartz can be shown to require that the illumination be as parallel as possible.

After much trial and error, it was determined that an optimum optical train consists of a large area, uniform light source concentrated on a pinhole placed at the focal point of a collimating lens, the light then passing

(4) Bond, W. L. and Andrus, J., Phys. Rev. 101, 1211, (1956).

(5) Indenbom, V. L. and Tomilovskii, G. E., Sov. Phys., Crystallography, 2, Transl. p. 183 (1957).

through monochromatizing filter, polarizer, quartz specimen, analyzer, and thence through a moderately long focal length lens for projection of the image the quartz plate onto film. Figure 1 shows the evolved train used most recently. The illumination source is a conventional G. E. Mazda 300 w S-4 mercury lamp with a diffuser glass in the helmet window. With a simple lens, the diffused light emitted by the glass is focussed onto a 0.05 cm dia. pinhole pierced through a blackened thin brass plate. It was found convenient to use a good quality, high aperture lens for collimation, in this case a Kollmorgen Ser. II, BX-163, F:2.0, 4-inch f.l. projection lens. A Baird-Atomic Type B-1 Multilayer Interference filter, peaked at 5461 Å. was used to eliminate the weaker Hg lines and "white" background. Polarizers in rotary mounts were the best available from Polaroid Corp. -- Type HN22c, Sp X XFE Glass Laminated Linear Polarizers 2" dia. Various inexpensive 2-element uncoated achromat lenses were used to focus the quartz plate image on either Panatomic-X or Tri-X Kodak 35 mm film carried by an Edixa camera minus lenses.

The camera is a single lens reflex type found most convenient for focussing and adjusting polarizer and crystal orientation by eye. For quartz plate specimens of high homogeneity, the image intensity with maximum background extinction is extremely weak. Dark adaptation of the eye was normally achieved after 10 minutes in total darkness. Even so, only the grosser features could be seen by eye; film exposure and subsequent enlargement or microscope examination always disclosed far more detail. Optimum exposure times varied widely; Z-cut plates when using Tri-X film required from 5 to 30 minutes, while non-Z plates were exposed for as long as 3 days. In all cases, of course, the completely darkened room acted as a camera box; egress to the room by people during open-shutter times was accomplished by (a) opening the door rapidly, (b) partly darkening the hallway, (c) painting the entire walls, ceiling and floor of the darkroom a dark-green matte, (d) facing the film away from the door.

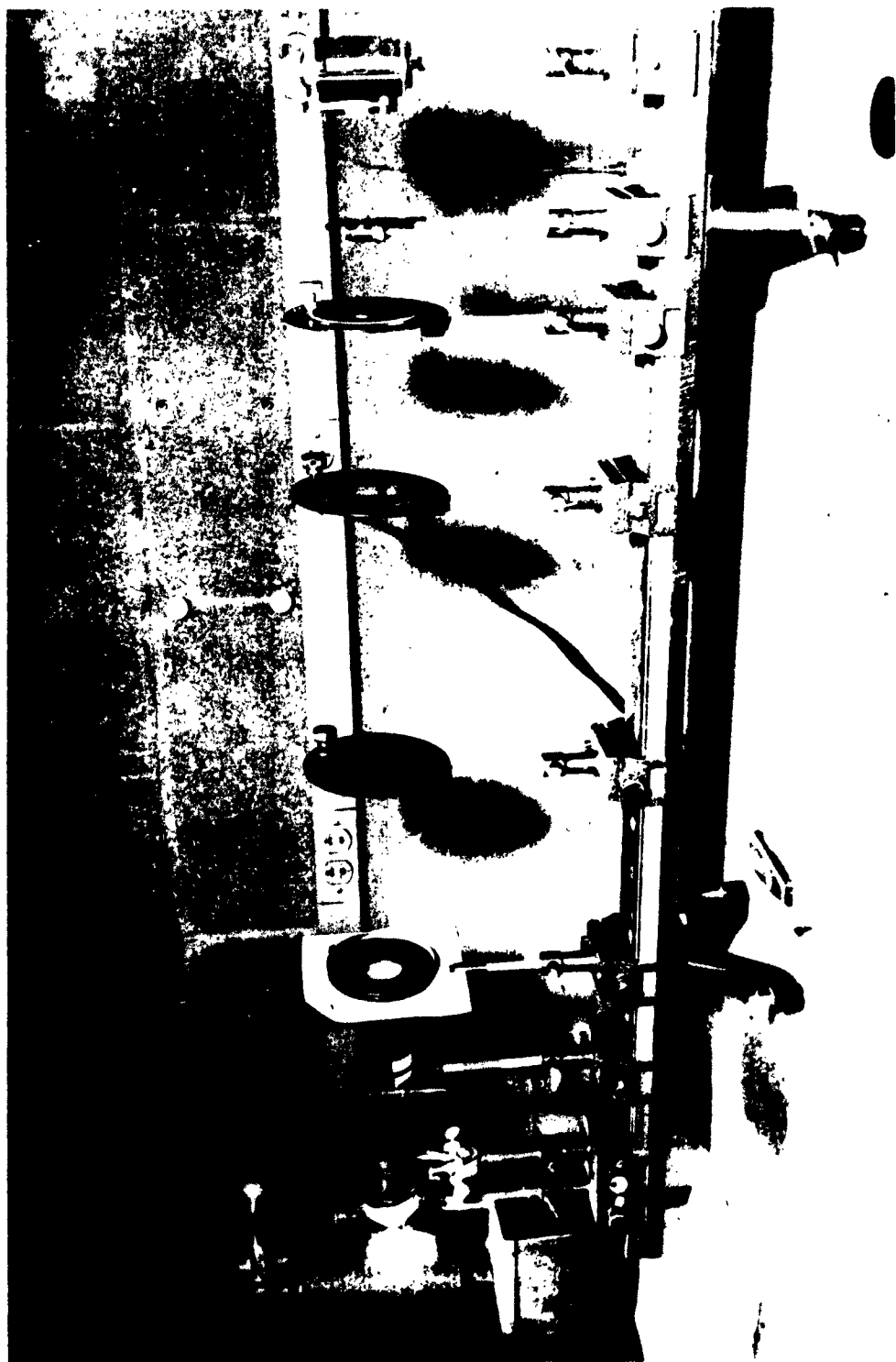


Fig. 1. Polarized light optical train.

A blackened paper box was placed over the light source assembly, with an opening for the pinhole, while all cracks were stuffed with black velvet.

The polished quartz plates are each mounted on a disc of black paperboard with a window cut to transmit light through the desired area. An unpatented but useful mounting cement was perfected* which combines the peeling quality of Carter's brand "rubber cement" with the dull black opacity of the automotive (true) rubber cement commonly used for repairing windshield leaks. Bothersome internal reflection from the edges of the quartz plates are greatly reduced by coating with this stuff. The paperboard mounts, cut to size, are in turn cemented to the Gaertner "Graduated Rotatable Object Holder." The components enumerated are mounted, in turn, on a standard type Cenco optical bench.

Quartz plates were prepared for study by first sawing blanks on a Reid Surface Grinder tooled with a diamond saw. Blanks were then lapped with #320 SiC grit on a P. R. Hoffman FR-3 Eccentric Lapping Machine sufficient to remove sawmarks and to make the opposing surface substantially parallel; this is followed by lapping with 3 micron grit on another set of lapping plates.

For a time we handpolished all plates with cerium oxide on a motorized polishing wheel; it was found that better polishing at less cost could be accomplished by the local branch of the American Optical Company.

4.2.1.2 X-ray Diffraction Contrast Methods

For several decades it has been realized that the strains arising from lattice imperfections can cause local variation in diffrac-

* Mix about 2 parts Carter's "Rubber Cement" with 1 part FoMoCo Rubber Cement 8A-19552-B, plus naptha solvent, if necessary, to give desired consistency.

tion intensity from single crystals. Lang⁽⁶⁾ was among the first to demonstrate a means for obtaining diffraction pictures of an entire crystal volume over a large area. This method is to be contrasted with the so-called Berg-Barrett⁽⁷⁾ technique wherein "back-reflection" yields a picture of only a relatively shallow region at one surface. This approach was used by this laboratory on two earlier contracts.^(3,8) Defect configurations could be seen, but their interpretation was hindered by the deficiencies of the techniques used.

The so-called Lang method utilizes the diffraction of X-rays through a large area of a uniformly thick crystal wafer, using a selected set of lattice planes in reflecting position; the incoming rays are ideally parallel and of uniform intensity, while the diffracted rays are recorded on a photographic emulsion ideally oriented parallel to the crystal wafer. The diffraction intensity from regions of strain near dislocations or other defects is increased over that of the "perfect" crystal, causing a kind of reversed shadow-graph of the defect strains on film. In practice, a large area beam cross section of X-rays of required uniformity and parallelism is not obtainable; thus, a system of collimating slits is used to form a scanning ribbon-like beam past which the crystal and film are simultaneously moved.

When we began our own efforts in this direction during the previous contact⁽³⁾, no commercially made Lang x-ray camera was

- (6) Lang, A. R., J. Appl. Phys. 30, 1748-1755, 1959; Jenkinson, A. E., and Lang, A. R., Direct Observations of Imperfections in Crystals, edited by Newkirk and Wernick, Interscience, 1962, pp. 471-495.
- (7) Barrett, G. S., Trans. A.I.M.E., 161, 15, 1945; Newkirk, J. B., Trans. Met. Soc., A.I.M.E., 215, 483-497, 1959.
- (8) Work by William R. Cook, Jr., reported by Hale, D. R. and Augustine, F., "Study of Methods for Improving the Quality of Synthetic Quartz," Contract DA-36-039-SC-72415, Final Report, October 15, 1958.

available.* Neither were there any published descriptions of hardware details that seemed adequate for designing and building our own. We knew that the half-height width of a typical quartz rocking curve reflection is about 5 seconds of arc. Therefore, if our X-ray beam chanced to be composed of ideally parallel and monochromatic rays, the translation mechanism would have to track the crystal within less than 5 seconds of angular deviation. Our first attempt to construct a Lang camera was based on a heavy milling head carriage. This was not successful. As described in the Final Report⁽³⁾ of that work, three large-area Berg-Barrett photographs were constructed by taking a series of separate static exposures across a quartz plate surface - then enlarging each, followed by cutting, matching, and pasting, to form a composite photograph. The results showed rather poor resolution,** required an enormous labor for each picture, and suffered from the inherent limitations of the Berg-Barrett depth penetration.

At the beginning of the present contract period it was elected to design and build the necessary mechanism for a Lang moving-crystal, moving-film camera, based on descriptions and photographs published by

* Erb and Gray Scientific (Division of Perkin-Elmer Corporation), 1103 Westgate Avenue, Oak Park, Illinois, is now offering for sale a "Lang microradiographic camera (scanning type)" made by Rigaku Denki Co., Ltd., 8 Kanda-Daidokoro-cho, Chiyoda-ku, Tokyo, Japan.

** We now know that considerable improvement would have resulted had we first etched away the polished surface zone.

Schwuttke⁽⁹⁾ . Additional and valuable assistance from Dr. Schwuttke in clarifying certain details of design and operation were subsequently obtained through private communication. The detailed mechanical design was carried out by Dr. David Parkinson, Advanced Development Division of Clevite. This work, and the cost of equipment and machining fabrication was borne by the Clevite Corporation, as was also the time our department personnel required for assembly and testing the finished camera.

The completed apparatus consisted of a Weissenberg X-ray camera (with the rotation drive disconnected) and the X-ray tube both mounted on a 700 lb. granite slab, together with a crystal goniometer, collimating slits, film holder, and a number of adjusting mechanisms.

In Figure 2 the camera and X-ray tube are shown in the foreground. The x-ray tube is connected via high voltage cable to the power supply portion of the Norelco X-ray unit in the rear. For crystal orientation before each exposure, the geiger tube (partially hidden at upper left on camera) is set at the required 2θ angle and its response fed to the chart recorder. The small rectangular box near the X-ray tube houses two reversible clock motors of 1 rpm and 4 rpm; these are used, with a connecting flexible cable, to drive the micrometer head on the crystal goniometer when obtaining resolved K α and K β peaks.

The X-ray tube is placed about 60 centimeters from the entrance or crystal slit of the camera. The columnar stand at the X-ray port supports a Soller collimating port slit assembly. The molybdenum target X-ray tube generates considerably higher energy radiation than does the copper target

(9) Schwuttke, G. H., Infrared Scattering Study, Final Report AFCRC-TR-60-157, Contract AF 19(604)-3482, April 30, 1969; General Telephone and Electronics Research and Development Journal, 1, 68-86, July, 1961; J. Electrochemical Society, 109, 27-32, 1962; Direct Observations of Imperfections in Crystals, edited by Newkirk and Wernick, Interscience, 1962, pp. 29-76.

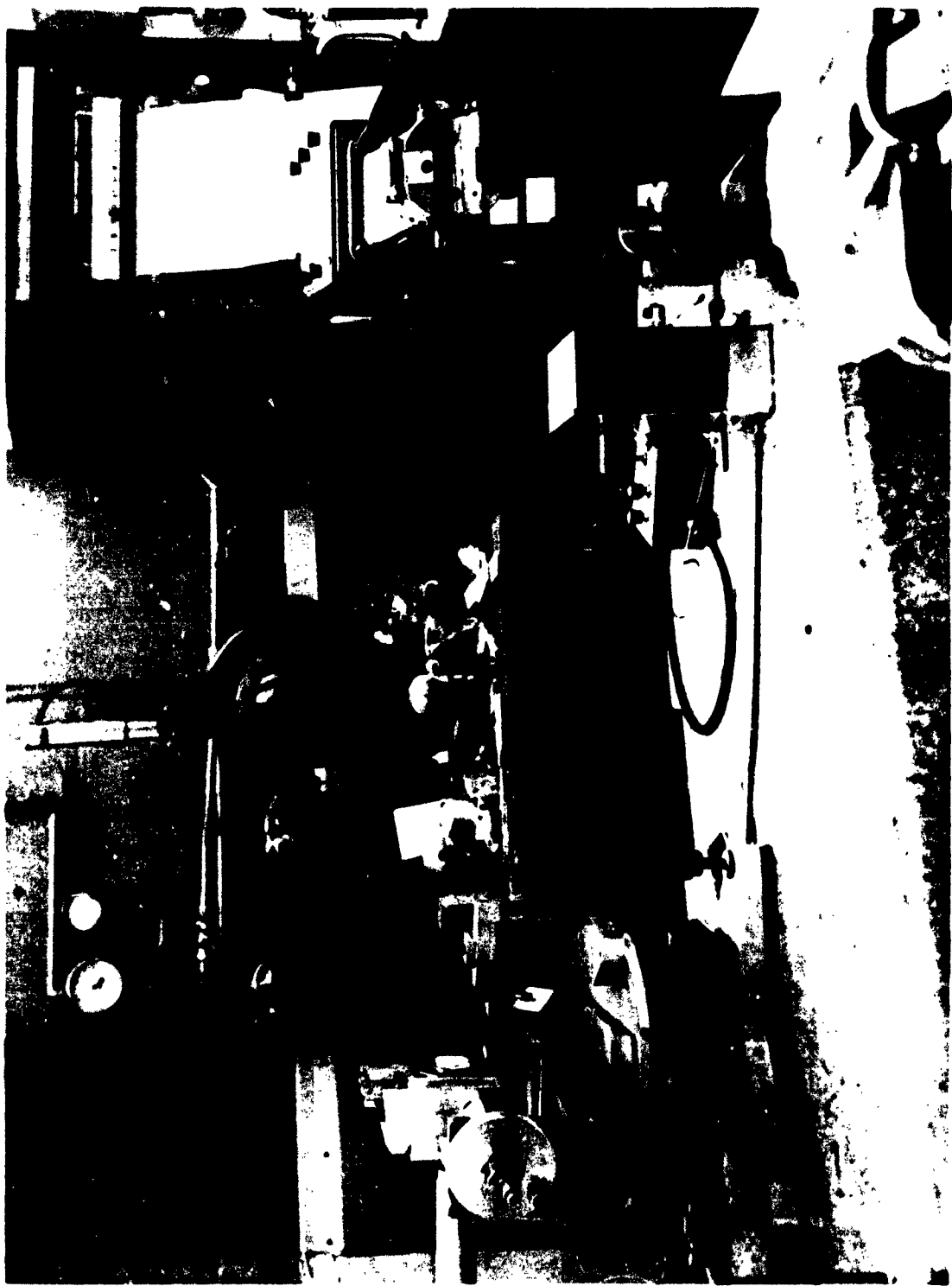


Fig. 2. Lang camera and X-ray tube mounted on granite. Lead shielding removed

tubes used for the work normally encountered by our X-ray section; as a result, the scattered radiation from slits and crystal was found to be stronger than the levels considered safe for continued personnel exposure. During normal operation a great deal of shielding with 1/16-inch lead is therefore used which has been removed for our photographic illustration. Also not shown is the spring damping mounting of the granite slab; this was designed to shield or damp all exterior vibrations higher than 1 1/2 cycles/sec. The slab further serves to minimize any orientation drift in X-ray reflection intensities that might ordinarily arise from loading strains and temperature fluctuations.

Figure 3 shows a quartz plate in place on the camera. Those familiar with standard X-ray diffraction equipment can discern the Weissenberg camera portion of the assembly; its sled bed and supporting graduated circle plates have been removed from the standard platform and placed on a larger plate. This plate is pierced with circular slots for mounting the entrance slit seen at left, and the geiger tube support. Translational adjustment is effected by the undersupporting set of double cross slides; leveling screws in the three-point base support are set in tapped inserts leaded into holes drilled into the granite.

The entrance slit is, in reality, a horizontal tunnel 2 inches long, 1 inch high and 0.004-inch in width. The width is obtained by clamping brass shim stock between steel plates. Schwüttke⁽⁹⁾ recommends 0.001 inch slit width for optimum resolution. For our commonly used quartz reflection ($10\bar{1}0$) $d = 4.26 \text{ \AA}$, and the resulting $Moo_1 - Moo_2$ separation is $\Delta\theta = 1.73'$. We calculated that in our Lang camera setup, the port slit would need to be about .010 inch wide to effect $\alpha_1 - \alpha_2$ separation if the crystal slit were 0.001 inch wide. In any case, while endeavoring to gain experience in peak-searching by temporarily keeping to a high intensity of impinging beam, we held the port slit at 0.060 inch and the crystal slit at 0.004 inch. We discovered that pictures



Fig. 3. Assembled Lang camera.

taken at the α_1 maximum nearly always showed no evidence on the emulsions of any image doubling. Besides, the crystal to film distance used was usually ~ 1.5 cm., $\Delta 2\theta$ (for $\alpha_1 - \alpha_2$) was $3.46'$, and the resulting separation in the emulsion is then $\sim .015$ millimeter - a dimension barely above published values for the theoretical limit of dislocation resolution by the method.⁽⁶⁾ Examination of our dislocation pictures shows that our achieved resolution is at least as good as those results published for silicon. As pointed out by Webb⁽¹⁰⁾ the most serious limit to resolution is apt to be due to the vertical divergence of the (horizontally) collimated X-ray beam, when (horizontal) collimation is anything less than theoretically perfect. Thus, any given point on a diffracting plane is reflecting a beam of X-rays shaped like a segment of a cone, the angular subtension of the segment being limited by the geometry of the collimating slits. We find from calculation that even with a crystal slit of 0.001 inch, the vertical length of the arc intercepted by the film would be ~ 0.3 cm, a very smeary effect. However, if this basic arrangement also includes Soller slits of 0.1 cm vertical spacing, the computed resolution error at the film emulsion is 25 microns; this was confirmed by our finding of a slight vertical "smear" of this order on the emulsion images. Figures 4 and 5 show two views of the crystal goniometer portion of the camera. The crystal is held with "red wax" on a plate rotatable on a horizontal axis. This adjustment is done manually, inasmuch as it was found that the uniformity of reflection intensity over the crystal is comparatively insensitive to errors in that adjustment, a range of 2 degrees or more being a practical limit of needed accuracy. Small spring clamps hold this mounting ring in place. Adjustment of crystal orientation around a vertical axis is, of course, setting of θ . The micrometer screw moves a spring-loaded lever hinged by a double-clamped leaf spring; a pin near the hinge, in turn, impinges against the end

(10)

Webb, W. W., Direct Observations of Imperfections in Crystals, ed. by Newkirk & Wernick, Interscience, 1962, pp. 29-76.

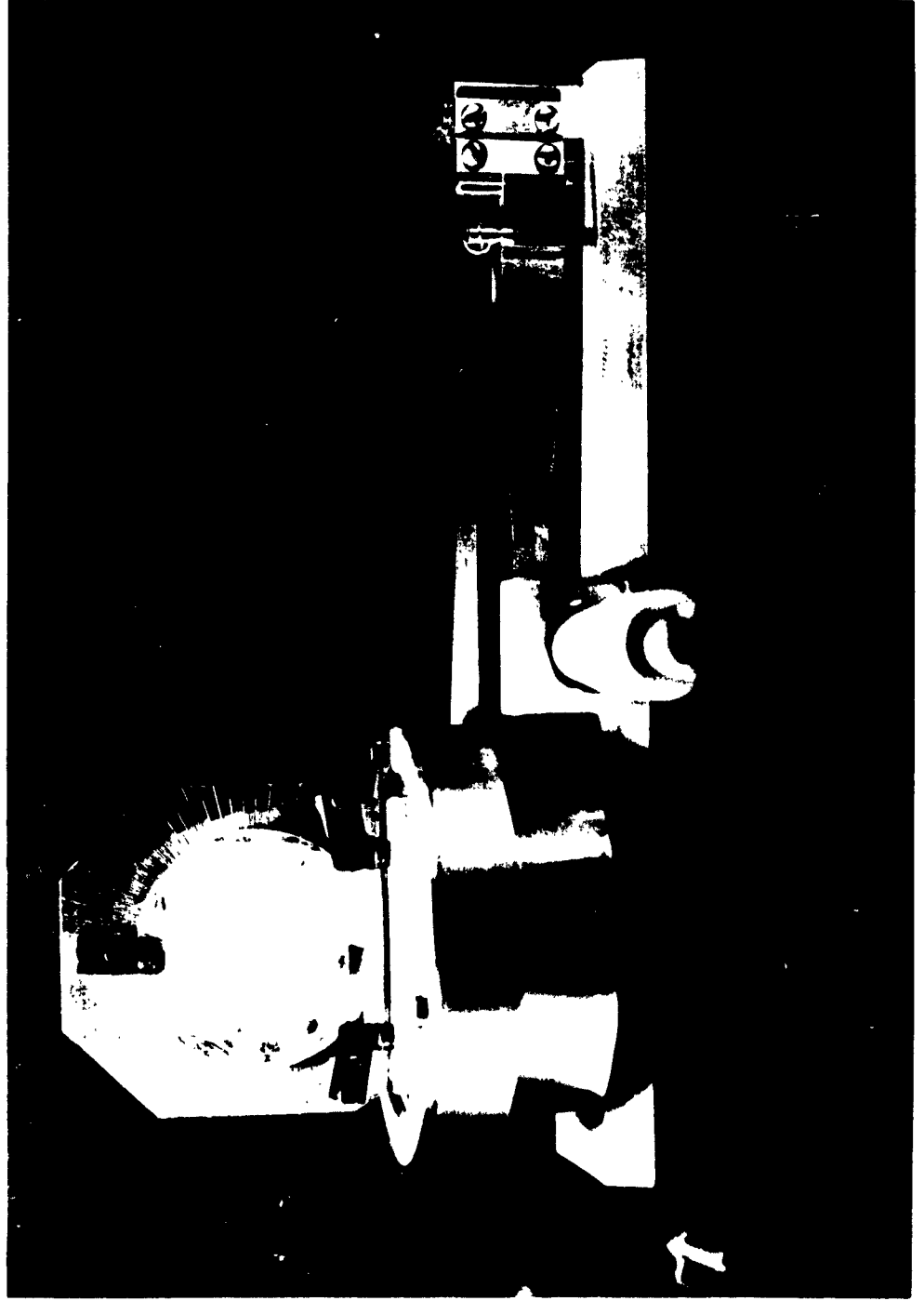


Fig. 4. Crystal goniometer. View along direction of X-ray beam.



Fig. 5. Crystal goniometer. Top view with film holder.

of a spring-loaded arm attached to the base of the crystal mount. The lever arrangement was so designed that 1/1000 inch of travel of the micrometer produces an angular change at the crystal of four seconds of arc. The rotary table support for the crystal holder turns on a lubricated, ground and lapped conical, gravity-thrust, bearing surface, where both bearing surface members are made from cast Meehanite. Most of the remaining machined parts of the camera are from free-machining aluminum.

The film holder is fitted with phosphor bronze springs, into which is slipped the emulsion plates, wrapped in black paper. These plates, about 1 inch square, were cut from 1 x 3 inch, 50 micron emulsion, Ilford Nuclear Plates, emulsion type G-5. As of late 1962, these must be ordered and shipped from the factory, Ilford, Inc., Ilford, Essex, U.K.

Handling and processing these plates requires some special precautions. The slightest scratch of the emulsion surface prior to actual fixing and removal of developer appears to catalyze subsequent "development" of the scratch. Cutting to size is done (under Wratten 6-B safelight) by scribing the uncoated side of the glass while the emulsion rests on a clean sheet of soft rubber; one then breaks across a wire fulcrum against the emulsion, great care being taken to avoid sliding the emulsion. The plate must then be protected on the emulsion side with a piece of thin rubber cut to size. When enclosed in the folded black paper for exposure the plate should be of a size such that the spring clips grasp the paper folds, but not the plate.

It was found that Ilford's recommended procedure for darkroom processing had to be slightly modified for our purposes. James Konishi of this laboratory worked out the following:

Since continuous agitation without any solid contact with the emulsion is necessary, a light-tight developing tank with a magnetic stirrer was devised. D-19 developer is diluted 1:1 with water. After 15 minutes development, the solution is discarded and fresh solution added for 15 more minutes developing. After this, in turn, is discarded, 5% acetic acid (stop bath) is poured into the tank for 10 minutes. At this point, all plates have a residual surface fog which must at this time be physically rubbed off without scratching the remaining emulsion. The only satisfactory means found was to use a small piece of wet chamois, kept between times in a jar of water. The plate is then returned to the tank and fixed in 30% plain hypo for 30 minutes; then discard and another 30 minutes in fresh hypo, followed by washing 2 hours or more in running water. At no time must any solution or water temperatures exceed 72°F, with all fluids maintained as close as possible to 70°F.

It was found that many developed plates were rather low in contrast when enlarged directly; it then became standard practice to enlarge first on to Kodalith Ortho-type 3 film, followed by enlarging as desired on regular photo paper.

During the course of the work it was determined that some low-contrast results could be ascribed to insufficiently etching away the polished surface layers of the crystals; 2 hours in 48% HF was finally determined as a minimum. However, Lang's rule of thumb⁽⁶⁾ gives the optimum crystal thickness as $\mu t \approx 1$, where μ is the linear absorption coefficient (calculated from Barrett's⁽¹¹⁾ table of mass absorption coefficients of elements) and t is thickness. When $\mu t > 10$, a reversal of contrast is effected, due to the Borrmann effect, in which dislocations appear as shadows (see ref. 6, 9, 10); (11) Barrett, C.S., Structure of Metals, McGraw-Hill, 1952; App. IV, p. 637.

at intermediate values of μt , one would expect cancelling effects tending toward zero contrast. For most of the quartz plates X-rayed, μt was from 1.5 to 2.5, with one or two near 4; for the thicker plates exposure times are longer and some reduction in contrast is observed, although still being "Lang" contrast (enhanced diffraction at dislocations). The requirement that $\mu t \sim 1$ leads, of course, to consideration of X-ray targets and crystal thickness. For quartz, calculation shows that for plates of a practical thickness of a millimeter or more, our commonly used copper target radiation is too highly absorbed and $\mu t > 10$. Our Norelco X-ray power supplies have a maximum operating voltage of 50 kv; a molybdenum tube becomes the most practical choice for quartz work. Since even a new high voltage cable tends to arc internally when operated near the maximum ratings, most of our exposures were made at 40 kv and 15 Ma current; under these conditions quartz plates having $\mu t = 2$ and a scanning travel of 2 cm required optimum exposure time of 15 to 25 hours.

In practice, the diffraction peak is roughly located by manually rotating the goniometer directly by its lever arm, while the geiger tube (Krypton-filled for maximum sensitivity to Molybdenum radiation) is preset at the calculated 2θ angle. The wide aperture of the tube makes this setting relatively non-critical.

(The lead cap seen in Fig. 3 is, of course, removed during these adjustments). When the sought-for reflection is manually located, the graduated clamp ring on the goniometer is used to make the peak fall within the range of the micrometer adjustment. Since the double lever arrangement gives 4 seconds of arc per 1/1000-inch at the micrometer, its total travel is conveniently over 1° . The peak is then traced out with desired resolution by driving the micrometer screw with one of the clockmotors; both $K\alpha$ and $K\beta$ peaks are run for verification. With the collimating slits used as described above, a typical $K\alpha$ peak has a half-height width of about 4 minutes of arc. After selecting the exact point on the diffraction peak desired, the back slit (between crystal and film) is adjusted for minimum width to still pass the diffracted peak from the entire length of

crystal traversed; this is done to reduce scattering and extraneous weak diffraction vectors, as well as stopping the primary beam. The desired limits of travel of the Weissenberg sled have first been set by the micrometer switch stops. The loaded filmholder is then dropped into place and the Weissenberg motor turned on. The time required for optimum exposure depends on (1) length of sled travel used, (2) strength of diffraction peak used, (3), emulsion speed, and (4) voltage and current to the X-ray tube.

4.2.2 Results

4.2.2.1 Introductory Discussion

During the course of this and the previous contract⁽³⁾ about 400 polarized light photographs and over 60 X-ray Lang-type photographs were taken of quartz crystal plates. It was found that the X-ray method reveals dislocation patterns with far greater resolution than does the optical technique. Regions of concentration of point defects, apparently because they introduce anisotropic lattice strain, are visible in both kinds of pictures. Just as dislocation strain fields cause imaging in both techniques, but with differences in physics, so are point defects differently manifested; the optical technique appears to show more detail in some cases. A disadvantage of the optics has been, however, that only Z-cut plates show any localized optical birefringence patterns; we do not yet understand why this is so. In contrast, we found that in quartz there is a sufficient number of strongly diffracting lattice planes that several possible crystal orientations each could be used for Z-, X-, Y-, and AT-cut plates. The polarized light technique has a useful advantage in needing only inexpensive equipment and yielding more pictures per day.

As described in the literature^(6,9,10) the intensity of augmented diffraction from a dislocation line is roughly proportional to

the component of the dislocation Burgers vector perpendicular to the diffracting plane. Since the Burgers vector of an edge dislocation is perpendicular to it (and in the glide plane) while that of a screw dislocation is parallel, one can deduce the kind of dislocation from a consideration of its image intensity and its angular relation to the diffracting plane. An unambiguous deduction frequently cannot be made from a single X-ray photograph; it is then useful to take additional exposures using other reflecting lattice planes. In the X-ray photographs that follow, it would be, from a rigorous point of view, desirable to show for each the geometry of the crystal plate, film plate, diffracting planes and X-ray beam. As a practical matter, however, (a) the diffraction planes used were roughly perpendicular to the surface of the quartz plate, (b) the reflection angle θ was less than 10° , and (c) the emulsion plate was set nearly parallel to the crystal plate. Where these generalities were seriously violated, such will be noted. The crystal slit apparently contained some entrapped metal particles whose shadows appear on the emulsion plates as a set of parallel thin stripes. These were found convenient as a means of scaling and orienting the developed plates, and were purposely left undisturbed. The traces of the diffracting planes are, in all cases, perpendicular to these shadow traces. As a rule of thumb for the reader, therefore, all visible features in the X-ray pictures must have an intensity proportional to a Burgers vector component parallel to these stripes. If a dislocation line is visible and perpendicular to the stripe pattern, for example, it must, therefore, be an edge dislocation. Furthermore, if it is interpreted as being strongly visible, its Burgers vector is not parallel to the diffraction planes being used.

4.2.2.2 Crystals having Q data

Run Clevite 54F-4 was grown on last year's contract with growing conditions described in Table II. The crystals were visually clean except for a layer-like region of differing refractive index formed during a power failure. In polarized light the defect strains appear rather weak (Fig. 6). Figures 7 and 8 are X-ray photographs of a Z-plate cut to include the power failure discontinuity within the plate and nearly parallel to the surface. Both X-ray exposures used $(10\bar{1}0)$ diffracting planes, the second being taken by rotating the crystal plate 60° from the first orientation about the horizontal goniometer axis. The dark undulating line in Fig. 8 is the outcropping of this region; in Fig. 7 it is barely visible. The crescent shaped halos are interpreted to be undulations in the power failure zone. The short streaks are dislocation lines ending at the two opposing plate surfaces, and inclined at small angles to the Z-axis. The patterns of streaks in the two pictures are not identical; this is partly due to the θ angle from the normal, at which the lines are projected, but also to the non-visibility of the lines whose Burgers vector lies in the respective diffraction planes. The 3-dimensional geometry of the streaks perhaps should be rigorously analyzed, inasmuch as they appear to consist of sets of parallel lines. Figure 9 is a Y-plate cut from the same crystal, using $(11\bar{2}0)$ diffraction planes. We see that most of the dislocation lines arise, fountain-like, from points on the Z-seed surface. The seed plate has obviously been cut through the seed plate of an earlier growth run. The few lines seen within the seed continue into the new Z-surface growth, sometimes apparently multiplying at the seed surface. Figure 10 is the same Y-plate, diffracted from $(11\bar{2}2)$ planes. The dark band here is the power failure discontinuity, nearly invisible in Figure 9; such a "blanket" of defects therefore has a kind of Burgers vector strain in a direction perpendicular to the "blanket." This appears to be a phenomenon similar to that exemplified by the oxygen-rich planes in sili-



Fig. 6. Clevite 54F-4 Z-plate with polarized light. 6. 7X.

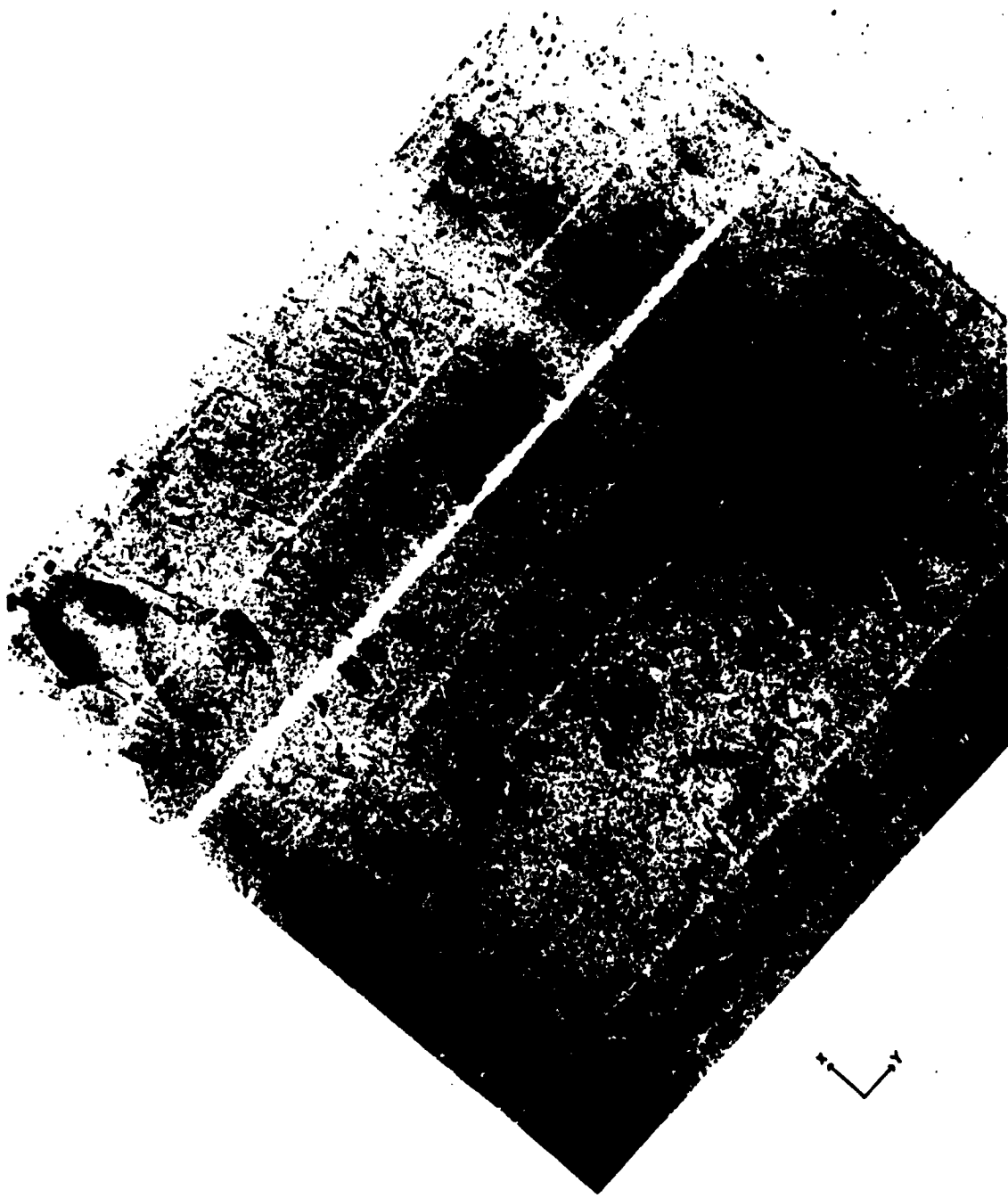


Fig. 7. X-ray diffraction photograph I of 54F4Zl. 9.3X. $\mu t = 1.7$.



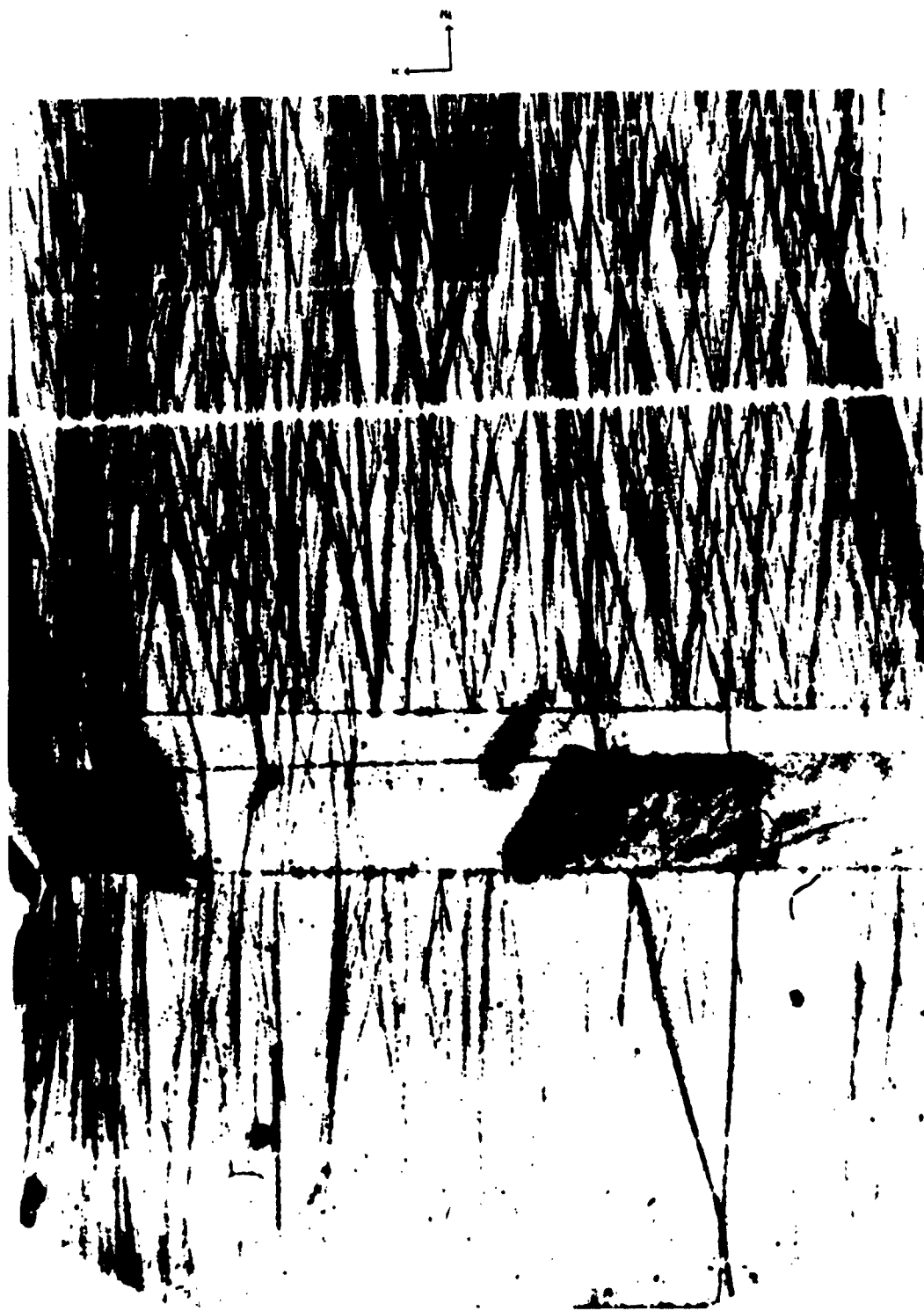


Fig. 9. X-ray diffraction photograph I of 54F-4Y1. 10X. $\mu t = 1.4$.

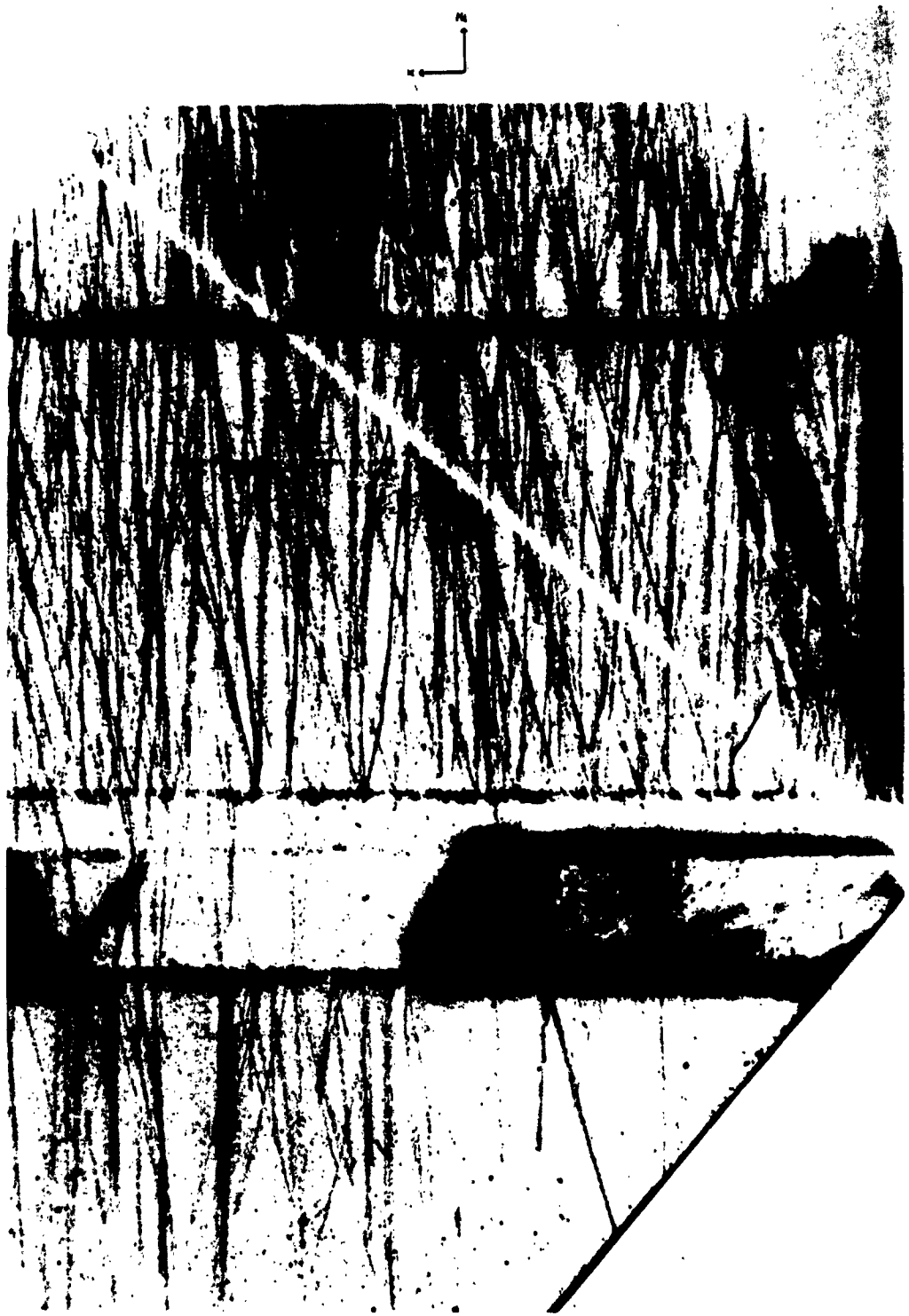


Fig. 10. X-ray diffraction photograph II of 54F-4Y1. 11.4X. $\mu t = 1.4$.

con crystals described by Schwüttke.⁽⁹⁾ This dislocation array continues without interruption through this region, with a few new lines being initiated there. A second, faint band in Fig. 10 can also be seen paralleling the darker one, nearer the seed surface. This is a second power failure scar that occurred earlier. These scars appear to consist of local concentrations of point defects; their chemical nature has not been determined. Most of the dislocation lines in Figs. 9 and 10 appear to fall into one of three sets of nearly parallel arrays, conforming to the sets of streaks in Figs. 7 and 8. In this crystal, and also in the others studied, the direction of the dislocations lie within an angle of 15° or less to the direction of growth. A count of lines crossing some arbitrary Z-plane in the Y-plate pictures gives about 800 dislocations per cm^2 .

Of the Bliley resonators made from 54F-4 crystals, one (H.H.A. Krueger's #1; Bliley label #4) was selected for X-ray study; its Q was about 1.5×10^6 . The top of the glass envelope was cut off at the green-glass supporting base, and the mounted resonator red-waxed at the glass envelope base to the goniometer, after removing the vertical crystal mounting support. Figure 11 shows the same features as the previous plates, but here the planes of the seed surfaces and power failure blankets are projected at an oblique angle. Figure 12 views the resonator after rotating it 90° in its own plane and using another set of diffracting planes. The Burgers vectors of the planar strain fields now parallel the diffraction planes and as a consequence the "blanket" features are only faintly visible.

The 54F-4 resonator was also X-rayed with and without removing its evaporated gold electrode, and before and after etching in 48% HF for 2 hours. No essential differences were noted. Presumably in fabricating precision resonators the polishing step introduces only a very shallow zone of damage.



Fig. 11. X-ray diffraction photograph I of 54F-4 resonator.
13.7X. $\mu t = 1.3$. (1011) Diffracting planes.



Fig. 12. X-ray diffraction photograph II of 54F-4 resonator.
12.3X. $\mu t = 1.3$. (11 $\bar{2}$ 0) Diffracting planes.

A contrasting case is next exemplified by SARP 4-17. While the polarized light photograph of the Z-plate in Fig. 13 shows rather intense points of strain, the X-ray photograph in Fig. 14 shows comparatively few dislocation segments, together with a pattern of broad, fuzzy halos. A resonator having measured Q of 0.5×10^6 was X-rayed (Fig. 15) in the same manner as the 54F-4 resonator. The source of the halos is now evident as a pattern of closely spaced growth bands, composed of varying concentrations of point defects deposited during growth on the Z-growing surface. These bands, when scaled back, appear to have a rather regular fine-structure spacing of about 5×10^{-3} cm, superimposed on a less regular, coarser repetition of intensity having a periodicity of perhaps a millimeter. The dislocation density was estimated at being from 100 to 400 lines per cm^2 .

Clevite 43B-4 was grown at low temperatures and pressures (299°C , 1500 psi) several years ago on Contract SC-64589, 1955-1956. Its Q was measured during the current contract as being $>2 \times 10^6$ at 5 Mc, room temp., and among the highest when measured at higher frequencies on another contract.⁽²⁾ Figure 16 is a polarized light photograph of a Z-plate cut through the seed, showing only the faintest birefringence strain above optical noise. Figure 17 is the X-ray picture of the same plate. The seed was free of dislocation lines, and the fast- and slow-X-growth has fewer dislocations than any of the many X-growth samples we examined. Other purely Z-growth plates from the same 43 B-4 crystal were examined with both polarized light and X-rays with similar results. Figure 18 is the X-ray of a Z-plate near the final growing surface; we cannot find more than about 25 dislocation lines per cm^2 .

SARP 7-19 was discussed rather fully in earlier quarterly reports from observations made only with polarized light. Figure 19 is a Z-plate cut through the seed, showing the intense banding in the fast- and slow-X-growth. Figure 20 is the X-ray of the center portion. The X-growth bands are invisible in this orientation, we are quite certain, because their strain Burgers vectors



Fig. 13. SARP 4-17 Z-plate with polarized light. 6. 8X.



Fig. 14. X-ray diffraction photograph of SARP4-17Z1.
11X. $\mu t = 2.7$.

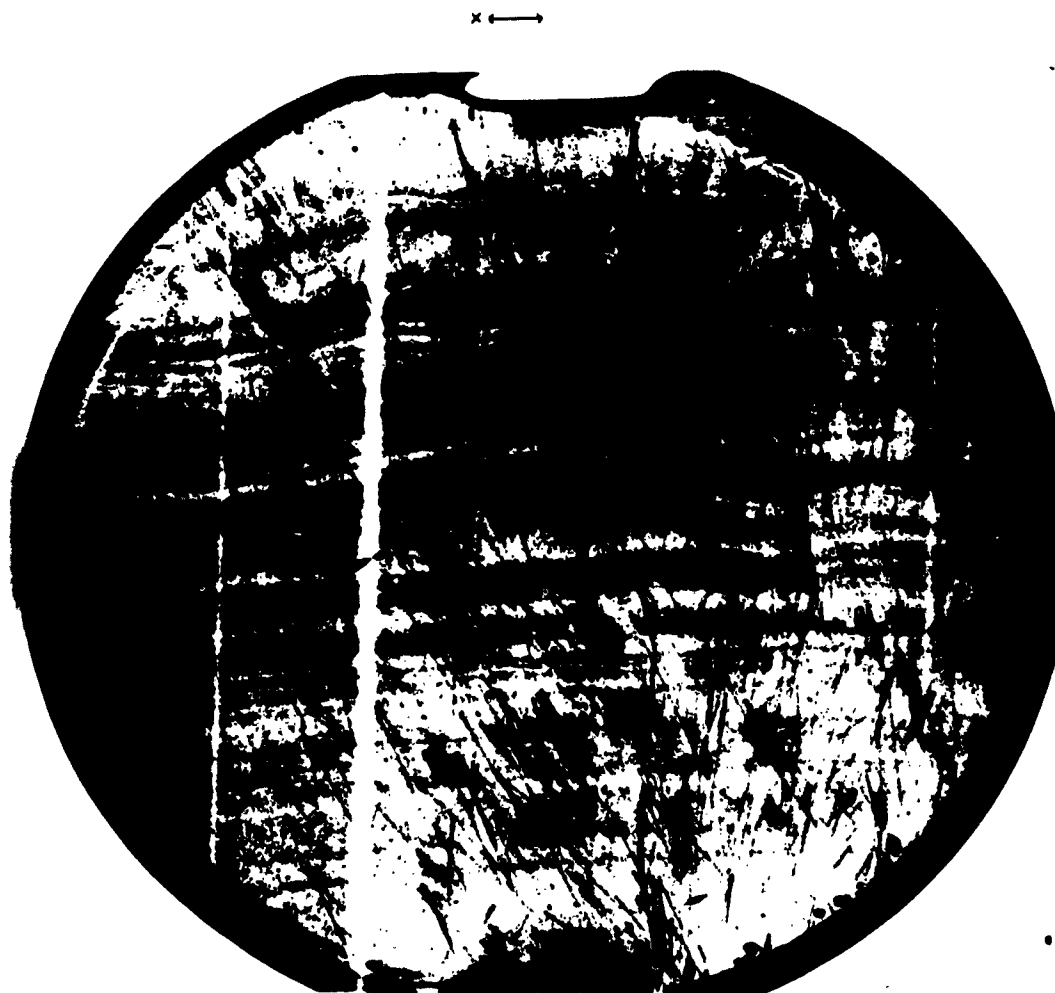


Fig. 15. X-ray diffraction photograph of SARP 4-17 resonator.
11.3X. $\mu t = 1.3$. (1011) Diffracting planes.



Fig 16. Clevite 43B-4-Z1 plate with polarized light. 8. 2X.

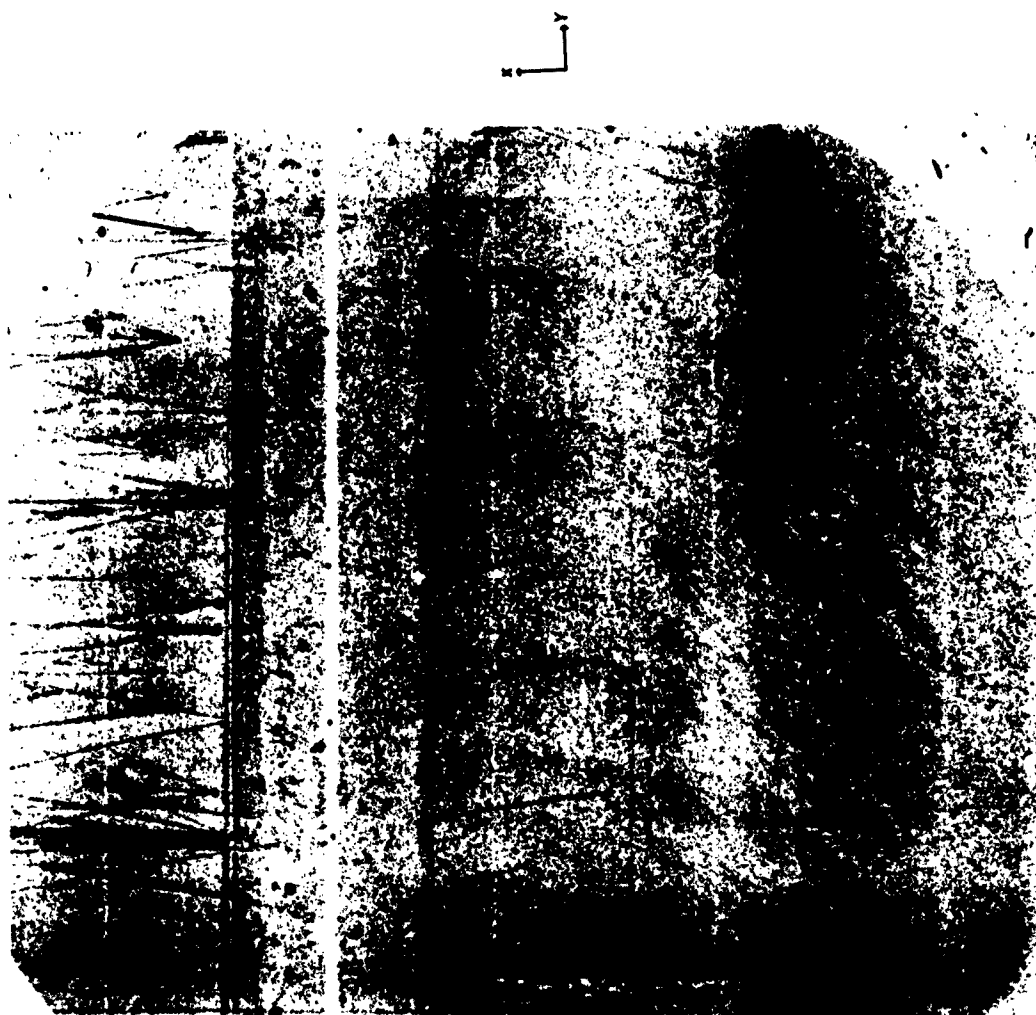


Fig. 17. X-ray diffraction photograph of 43B-4Z1. 13.8X.
 $\mu t = 2.1$.

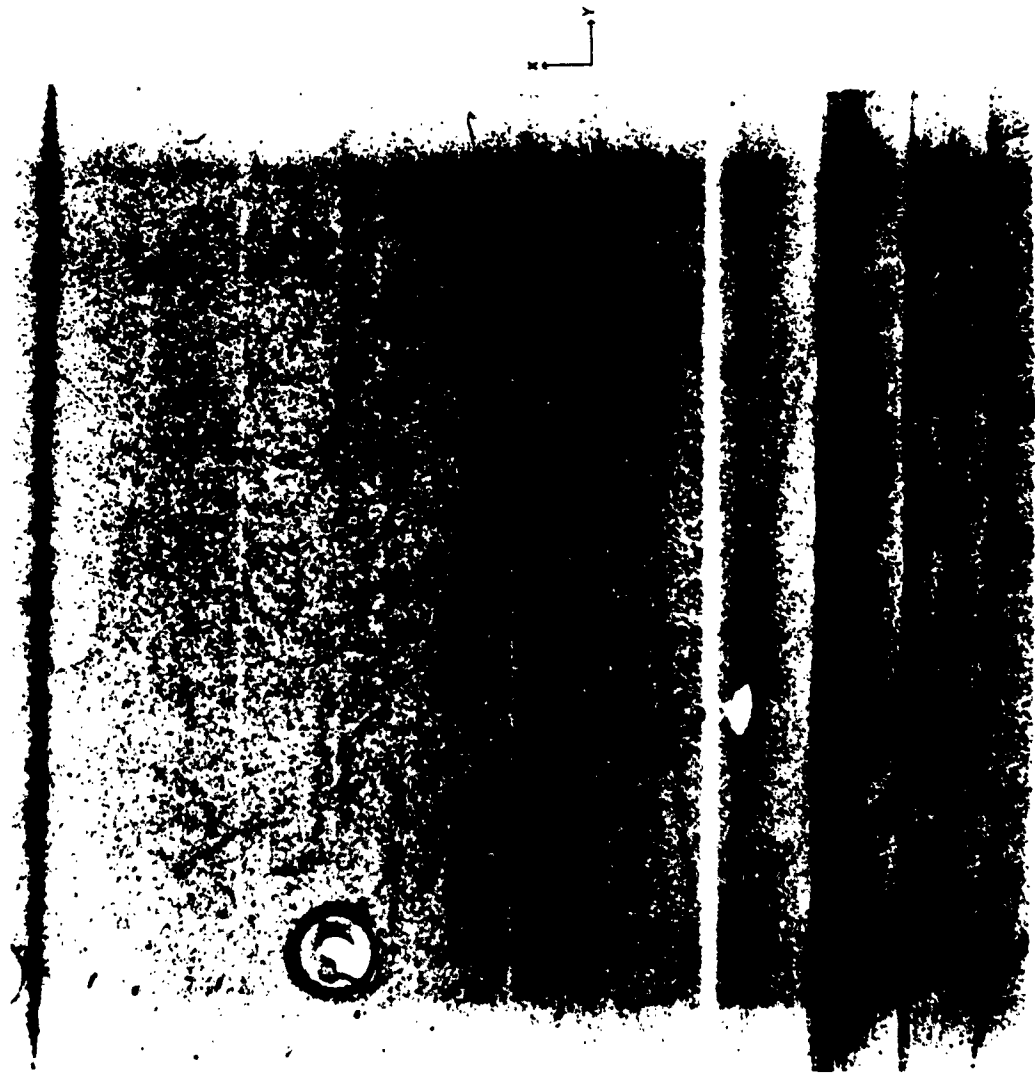


Fig. 18. X-ray diffraction photograph of 43B-4Z3. 10X.
 $\mu t = 1.9.$



Fig. 19. SARP 7-19Z3 plate with polarized light. 6.3X.

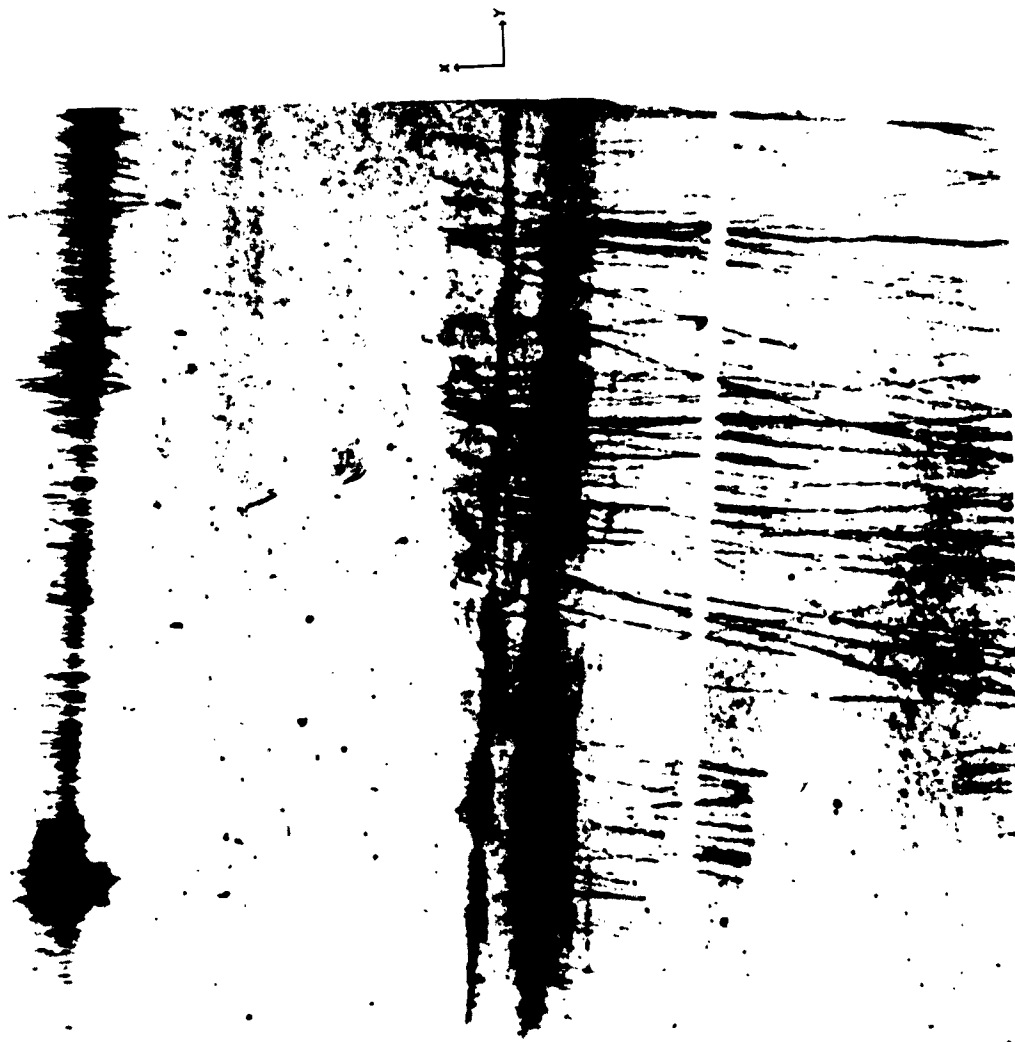


Fig. 20. X-ray diffraction photograph of SARP 7-19Z3.
10X. $\mu t = 2.4$.

almost certainly lie in the X-direction and thus would not affect diffraction from the $(10\bar{1}0)$ planes used, which were also parallel to X. In the Second Quarterly, it was pointed out that the X-growth banding in these plates, as well as the central Z-growth area, is slightly biaxial. This recalls some of the observations in natural quartz by Bambauer, et al.⁽¹²⁾ The plane of the pair of optic axes corresponding to the two optical melatopes has a Y-Z orientation in the X-growth and an X-Z orientation within the Z-growth. Further, the direction of the bisector of these axes varies its direction from band to band within the X-growth. From the optic figure in a petrographic microscope it was determined⁽¹³⁾ that the maximum 2V angle between the optic axes was about 3° .

Figure 21 is one of the polarizing light photographs of SARP 7-1925, cut near the outer growth surface, oriented for extinction of the fast-X region to show banding, while Fig. 22 is oriented to also show Z-growth extinction. Figure 23 is the X-ray photograph; dislocation density in the X-growth is much less than in the material adjacent to the seed. Also to be noted is a diagonally oriented growth banding or streaking that is visible in both polarized light and X-ray photographs. Dislocation line densities were estimated to be $100/\text{cm}^2$ in Z-growth and $200/\text{cm}^2$ in the worst X-growth. The measured Q was 1.4×10^6 .

SARP 5-38 showed a Q of 1.1×10^6 . Figures 24 and 25 are polarized light and X-ray pictures, respectively, of a Z-plate. Dislocation density in Z is $\sim 25/\text{cm}^2$ and apparently zero in X-growth. In both views, however, some halos in the Z-growth can be seen, that are, we believe, evidence of the type of Z-growth banding seen in the SARP 4-17 resonator. Foster and King⁽¹⁴⁾ obtained a

(12) Bambauer, H.U., Brunner, G.O., and Laves, F., Zeit. f. Krist., 116, 173-181, 1961).

(13) Using monochromatic light and an objective of N.A. 0.25, and calculation using the method given by Crystals and the Polarizing Microscope, 3rd Ed., Hartshorne and Stuart, E. Arnold, Ltd., London, p. 325-326.

(14) "Fundamental Studies of the Properties of Natural and Synthetic Quartz Crystals," Second Interim Report, 23 February, 1961, Contract DA 36-039-sc-85365, J. C. King and N. F. Foster, Bell Telephone Laboratories.

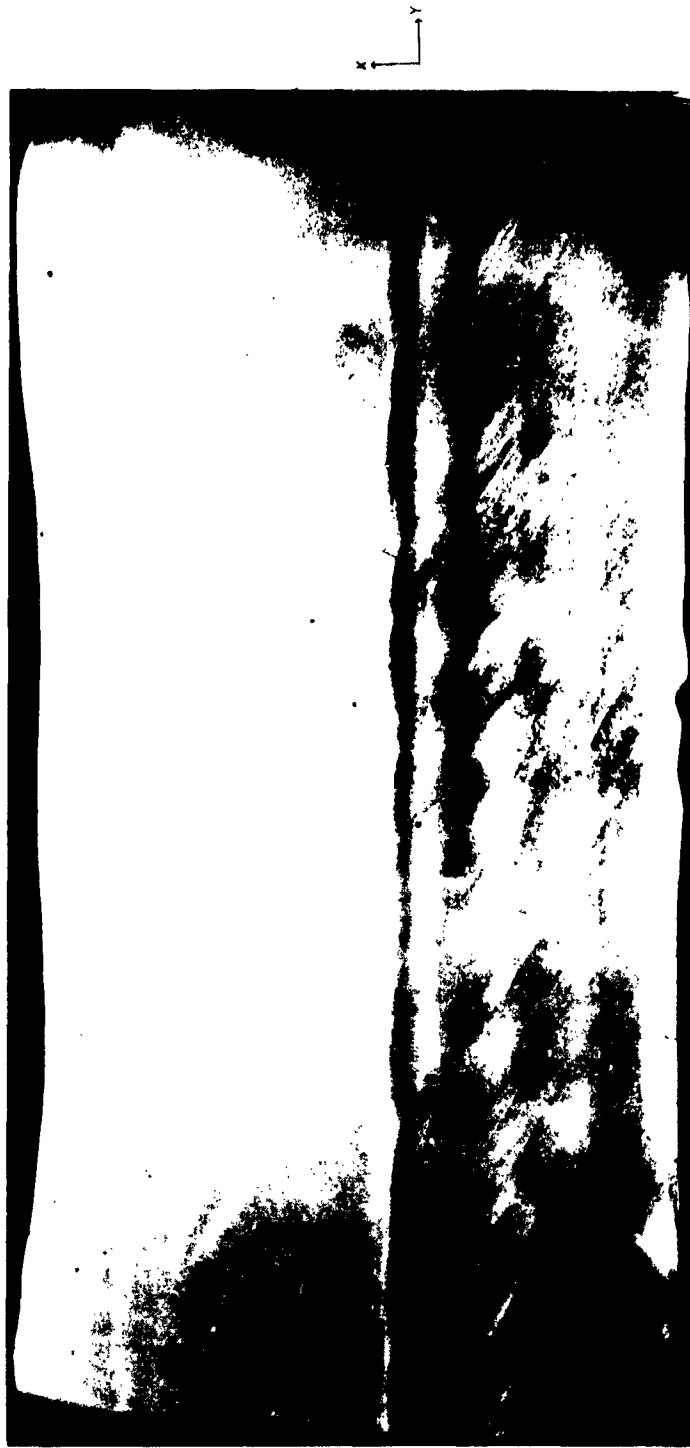


Fig. 21. SARP 7-19Z5 with polarized light to show fast-X growth banding. 5.8X.



Fig. 22. SARP 7-19Z5 with polarized light to show Z-growth extinction. 6.3X.

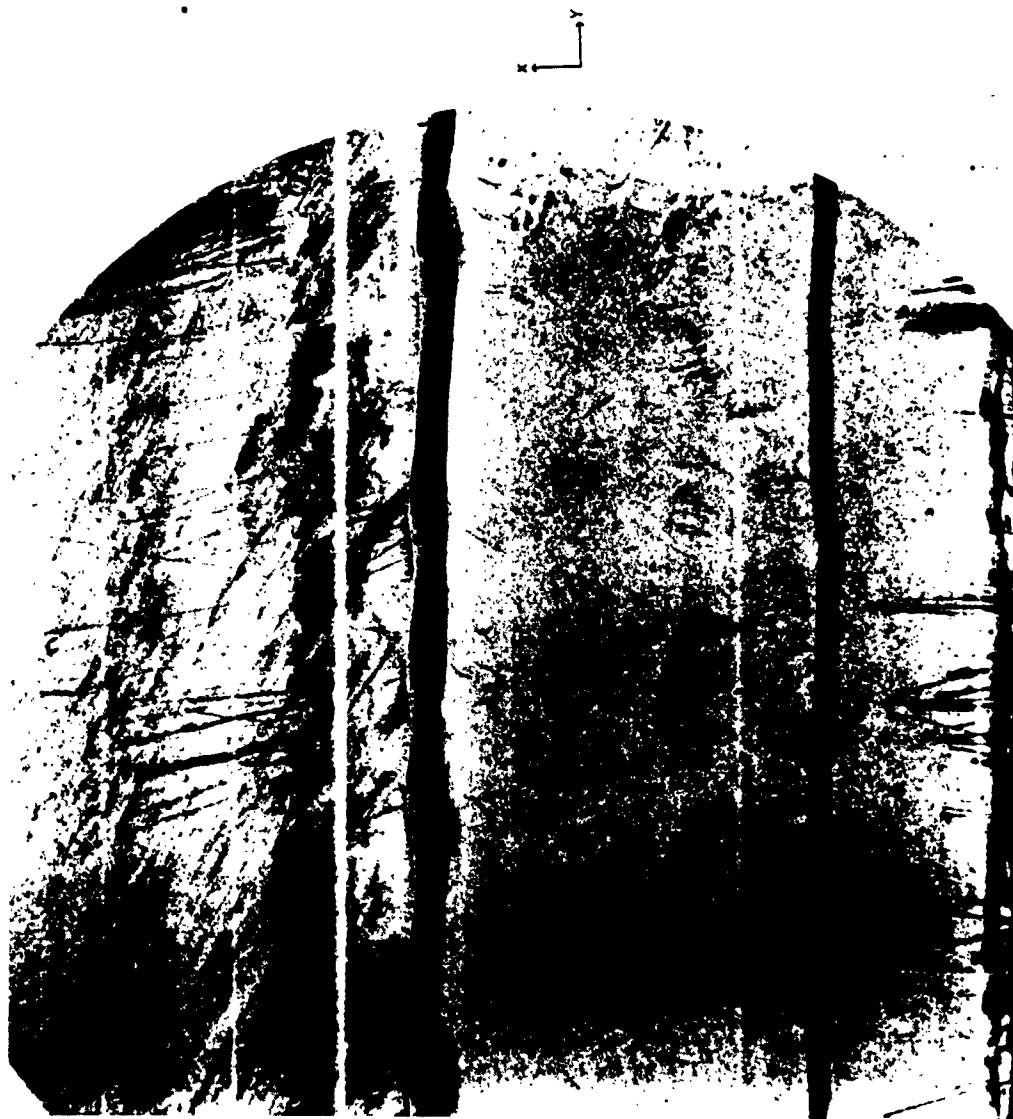


Fig. 23. X-ray diffraction photograph of SARP 7-19Z5.
9X. $ut = 1.7$.



Fig. 24. SARP 5-38Z1 with polarized light. 6.5X.



Fig. 25. X-ray diffraction photograph of SARP 5-38Z1.
10X. $\mu t = 2.4$.

similar pattern in Z-growth as a darkening by electrodiffusion with silver.

The Western Electric crystal selected for resonator fabrication was also, in part, sliced up and photographed by polarized light and X-rays. The surface of the seed plate was marked by a zone of visible liquid inclusions. The outermost slice, W.E. Z6, in polarized light, is given in Fig. 26, and with X-rays in Fig. 27. The felt-like dislocation pattern is difficult to count, but it shows well over 1000 lines/cm². Q was poor, being $< 0.5 \times 10^6$ at room temperature. This crystal shows clearly that if growing conditions are such that many crevasses and liquid inclusions are initially formed at the seed surface, a high dislocation content will result.

Other crystals for which some Q data exist were also examined. Krueger⁽²⁾ earlier found that Western Electric 23-13 had high Q in the 100 Mc ranges. Dislocation concentration was found to be somewhat nonuniform and about 500/cm² in Z-growth. On the same contract⁽²⁾ Krueger found that Clevite 54B-5 (X-growth) gave poor Q in the 100 Mc range; our X-ray picture of a Z-plate (composed entirely of fast X-growth) showed a very high dislocation density of from 1000 to 5000 lines/cm².

Clevite 54C-6 yielded a series of Z-plates having highly intense and localized birefringence strain patterns. X-rays showed that these are due to concentrations of dislocations localized as subgrain boundaries. Full discussion and photographs were given in the Third Quarterly Report, as also were other illustrations of the correspondence between optical and X-ray images of dislocation arrays.

4.2.2.3 Miscellaneous Observations

As reported in the Third Quarterly Report, Clevite 50J-1 appeared to be entirely free of dislocations, although the Z-plate examined contained a portion of the original natural-quartz seed plate. This seed plate portion was manifested as a pattern of concentric hexagon segments formed as impurity banding on natural quartz prism faces. The plate was subjected to a designed bending stress of from 1/3 to 1/2 the breaking stress while heated overnight at 550°C. The exper-

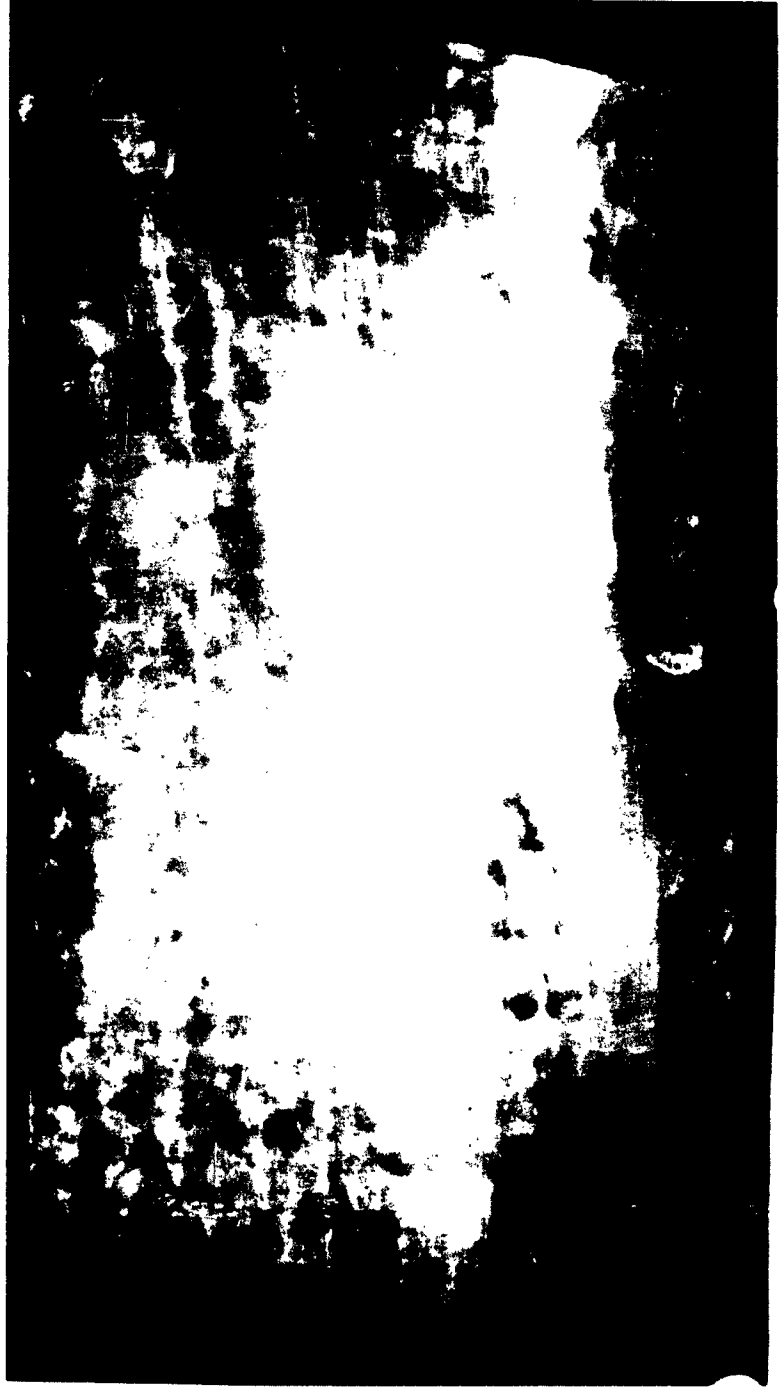


Fig. 26. W. E. Z6 plate with polarized light. 7X.



Fig. 27. X-ray diffraction photograph of W. E. Z 6. 10X. $\mu t=2.6$.

iment was intended to show if any edge dislocations (parallel to X with Burgers vector along Y) could be induced by glide. The plate did fracture along the line of maximum bending moment during the treatment. Figure 28 is an X-ray of a fragment along the fracture; no new (or old) dislocations are seen. This seems to confirm Sosman's⁽¹⁵⁾ conclusion that in general plastic flow does not occur in quartz, even at high stresses and high temperatures. The prismatic banding is clearly seen.

Plate Z2 of the 50J-1 crystal was also X-rayed. One face comprised an as-grown Z-surface, finely pebbled. The X-ray picture (Fig. 29), taken after carefully etching the opposing saw cut face only, shows a corresponding pebble-grain pattern of strains. After also etching the Z-growing surface 2-1/2 hours and again X-raying (Fig. 30) most, but not all, the pebble has gone, disclosing an interior free of dislocations, but containing another portion of the natural quartz seed plate. The conclusion to be drawn is that the slight growth that takes place during autoclave cooling carries with it a very high concentration of point defects. This is the same process observed in Clevite 54F-4 to result in "power failure discontinuities." One wonders if the regular growth-banding, such as shown in the SARP⁴-17 resonator, is not merely a milder form of the same phenomenon, caused not by drastic cooling, but by regular and comparatively modest temperature cycling during normal growth. It is assumed, of course, that such banding also requires the presence of impurities in solution; however, one should not rule out the possibility that the point defects are vacancies in the lattice.

Other crystals of interest were also X-rayed. Plates from the high purity runs Clevite 50K-3 and Clevite 54C-7 were both cracked during growth.

(15) Sosman, R., Properties of Silica, Chemical Catalog Co., (1927), p. 478.

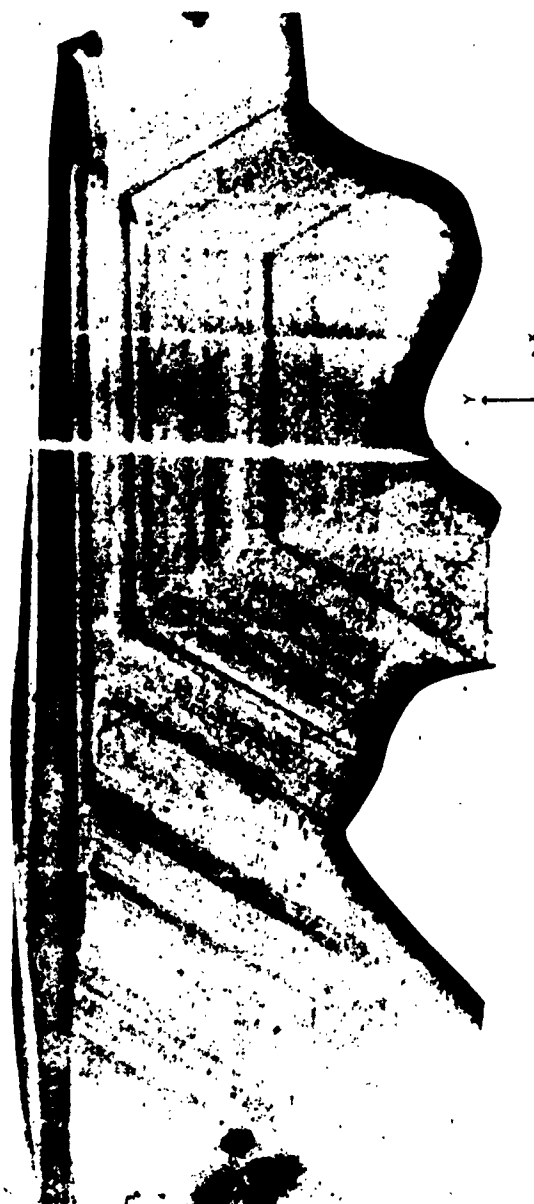


Fig. 28. X-ray diffraction photograph of fragment of Clevite 50J-1
plate Z1. 10X. $\mu t = 1.6$.

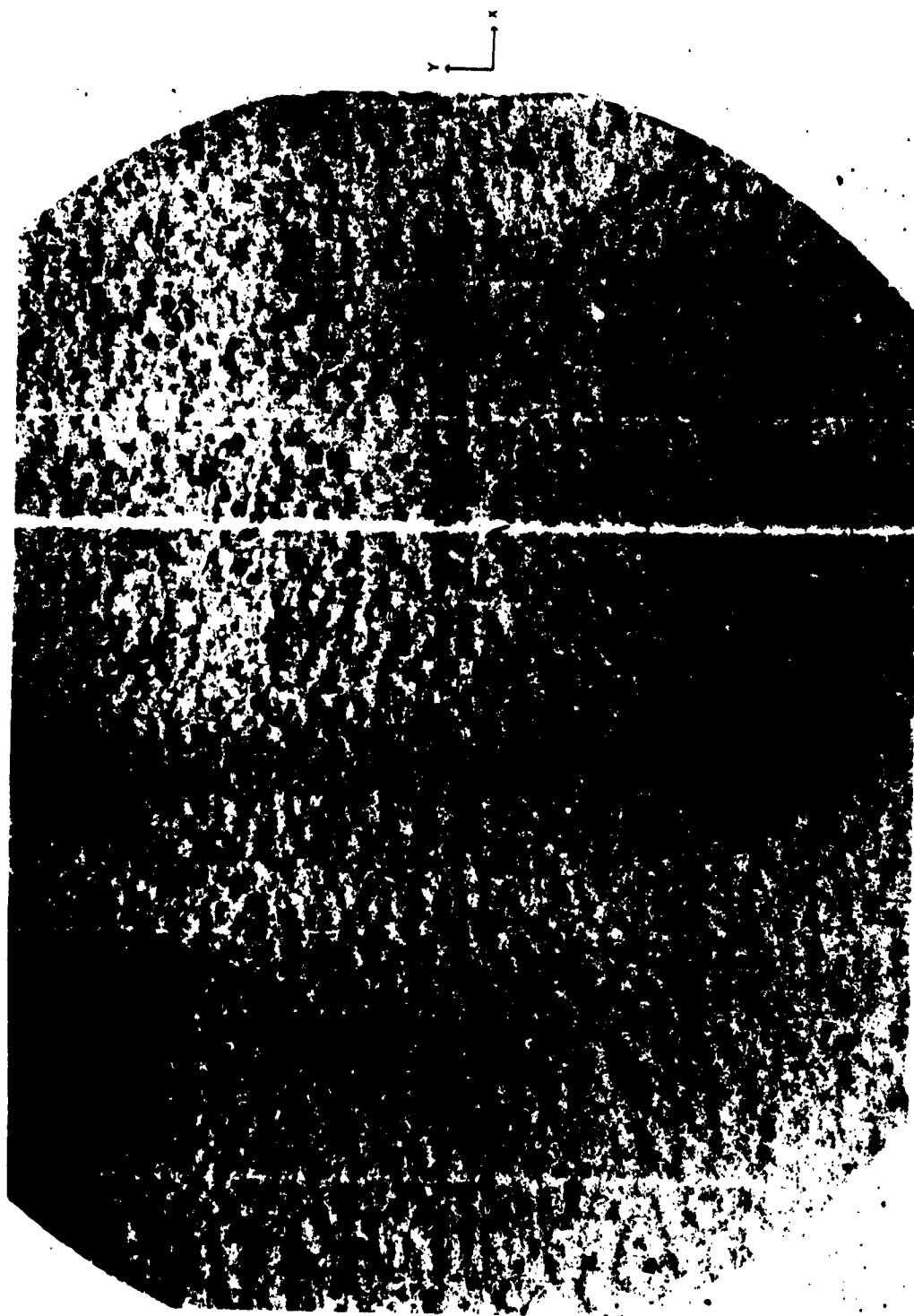


Fig. 29. X-ray diffraction photograph of Clevite 50J-1Z2 before etching the as-grown Z-surface. $9.6\times$. $\mu t = 3.0$ to 3.5 .



Fig. 30. X-ray diffraction photograph of Clevite 50J-1Z2 after etching the Z growing surface. 9.4X. $\mu t = 3.0$ to 3.5.

In 54C-7 a high dislocation content was found. The fracturing in 50K-3 was found to be associated with regions of intense strain that obscure any dislocation line images that might be present.

Clevite 44E-13 was an old aluminum-doped run. Both polarized light and an X-ray picture show a Z-plate to have a high dislocation density.

When Clevite 54B-4 (plate XU-18) was first X-rayed after the usual 2-hour etch, the image seemed rather poor. X-cut surfaces, such as this, etch very slowly, and the plate was etched again, for 18 hours, with the hope of removing any remaining polished layer. When then examined, it was found to have suffered little surface etching, but the plate was shot through with extremely fine hair-like tunnels extending completely between major surfaces. Their pattern was identical to the previously obtained X-ray dislocation pattern.

On a previous contract⁽⁸⁾ Augustine grew quartz on a Z-face cut with shallow sawcut grooves. X-irradiation of the crystal disclosed darkened "feathers" arising from each groove when seen in cross section. We etched and X-rayed the same X-cut sample. Figure 31 is an enlarged reproduction of a part of a photograph (from that report⁽⁸⁾) made by simple light transmission; Figure 32 is our X-ray picture of the same portion of the crystal. The X-ray diffraction discloses a detailed strain field pattern in each "feather", due to unequal distribution of point defects. As disclosed on the previous contract⁽³⁾ in discussion of Clevite 42B-10, the strain pattern was almost certainly present before irradiation darkening.

4.2.3 Infrared Absorption

The infrared absorption of quartz in the region of 3 microns contains bands which are due to hydrogen^(16,17). Measurement of the absorption is therefore an excellent tool with which to determine the presence as well as the condition of hydrogen in the crystal. Since most, if not all, synthetic and

(16) Kats, A., Thesis, Hydrogen in Alpha Quartz, Philips Res. Repts., 17, 133-279 (1962).

(17) Brunner, G., Wondratschek, H., Laves, F., Zs. für Electroch. 65, 735-50 (1961)



Fig. 31. Transmitted light photograph of Clevite 42B-13
X-plate 6-1 showing irradiation darkening of growth
on grooved seed. 7.8X.

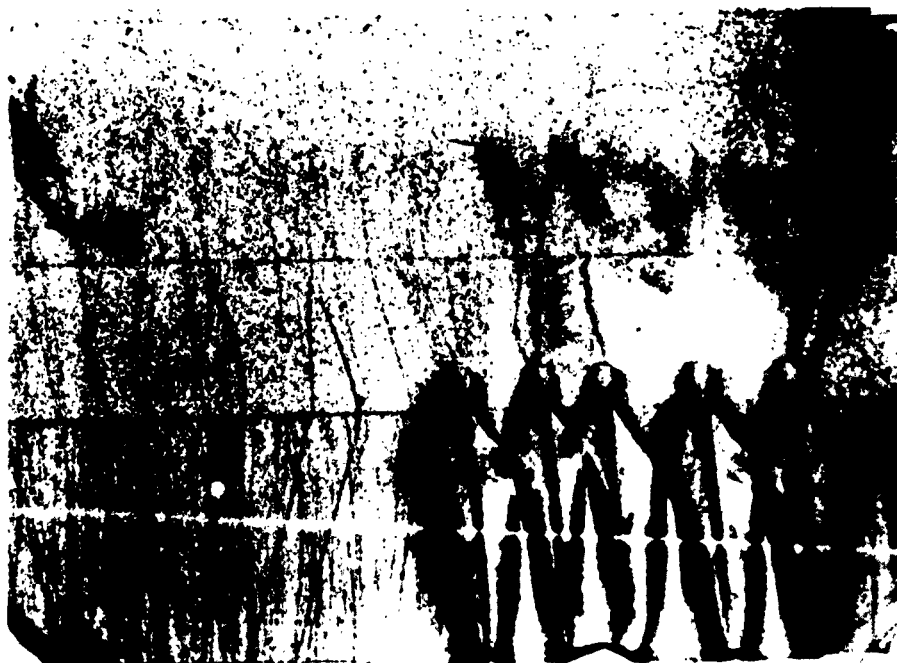


Fig. 32. X-ray diffraction photograph of crystal in Fig. 31.
7X. $\mu t = 2.1$.

natural quartz are grown in the presence of water, hydrogen must be considered as a principal impurity. A direct effect of hydrogen on Q of quartz seems to be contradicted by the work of King, Wood, and Dodd⁽¹⁸⁾, but this conclusion was not fully accepted in Europe in 1962 (Iaves, personal discussion). Time available for infrared studies under the current contract was quite limited. The crystal most thoroughly studied, from Run 54F-4, showed the principal H absorption of natural quartz much reduced, and no new absorptions (see Fig. 33). This indicates that the crystal had a lower H content than typical natural quartz.

Measurements were made on a Perkin-Elmer Spectrophotometer, Model 12G. The resolution of the instrument is about 0.1 cm^{-1} . Slit width was about $3 \times 13 \text{ mm}$. A demountable dewar sample holder was constructed for liquid nitrogen temperature measurements. Because of difficulties with this device the low temperature readings were made at about -57°C for the natural, -70°C for the synthetic.

In the figure are shown the measurements on the natural and synthetic materials at room temperature and at low temperature. The peaks of absorption occur at about the following wave numbers (cm^{-1}):

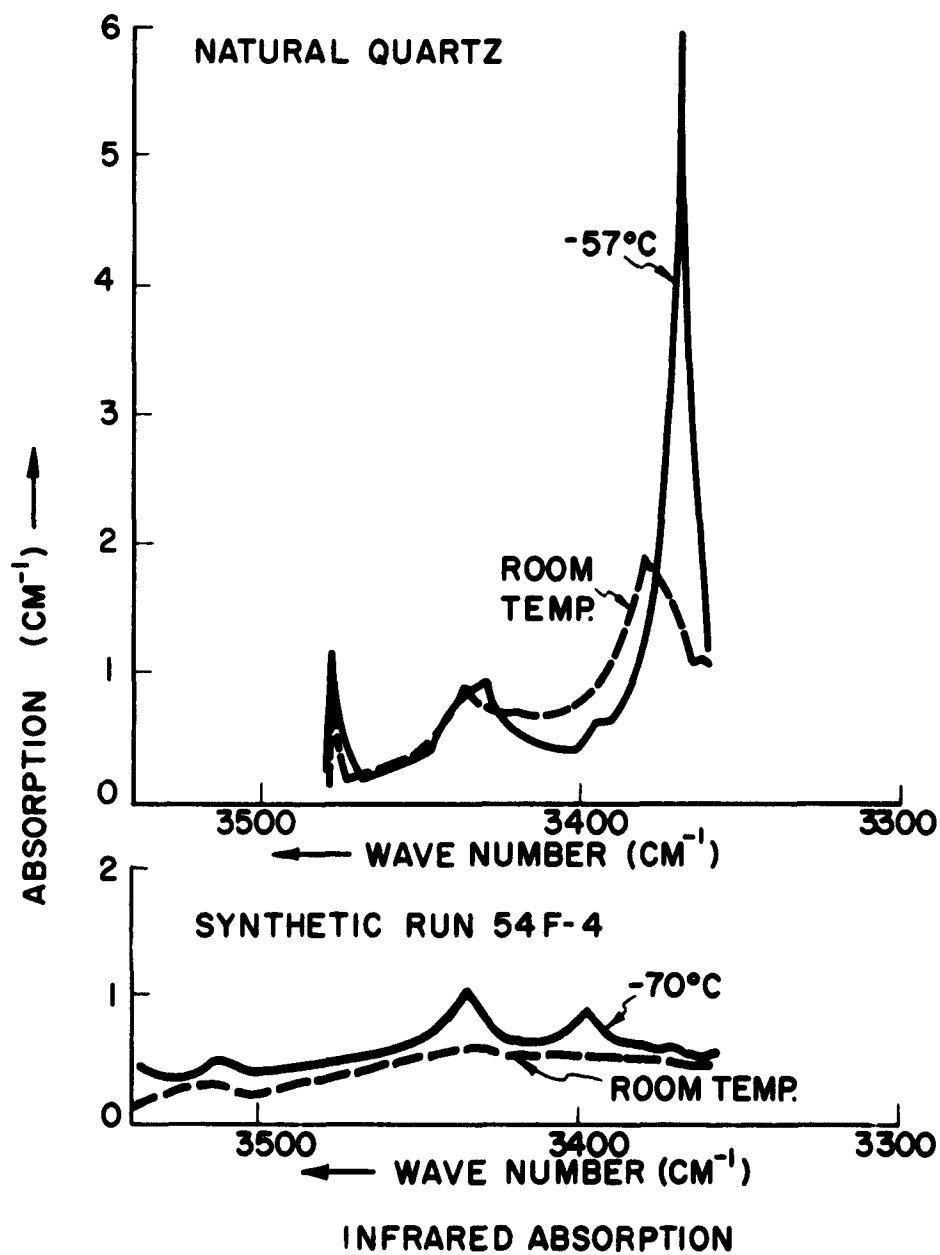
NATURAL		RUN 54F-4	
RT	-57°C	RT	-70°C
3478	3478	3520	3514
3435	3430	3430	3435
3381	3369	-	3397

Three characteristic peaks appear at 3435 , 3370 and 3311 cm^{-1} in natural quartz, and in synthetic quartz grown at high pressure (Kats, Ref. 16, p. 264). The measurements shown above were taken through the range 3311 cm^{-1} for the natural quartz and this particular peak was very low. It is believed that for Run 54F-4 the peak would not show.

Since the 54F-4 was measured at a lower temperature than the

(18) King, J., Wood, D., Dodd, D., Phys. Rev., Letters, 4, 500 (1960).

FIGURE 33.



natural and yet exhibits lower peaks, the conclusion may be drawn that the synthetic is freer of hydrogen.

54F-4 shows a relatively high peak at 3396 cm^{-1} . This peak has been identified with Li by Haven and Kats⁽¹⁹⁾ (see Figs. 1 c and 1 e).

Wood⁽²⁰⁾ found that the IR absorption in the 3μ region for three types of quartz growth in a Y-bar crystal diminished in the following sequence: slow-X > r > Z. Since the acoustic absorption diminishes in the same sequence, the hypothesis arises that the absorption is a direct function of the hydrogen content. King, Wood, and Dodd⁽¹⁸⁾ determined, however, that high temperature electrolysis increases the optical absorption due to OH and simultaneously causes the acoustic absorption peak at 50°K to vanish. They concluded that the protons in quartz (compensating the substitutional aluminum atoms) are not responsible for this peak. However, the essential result of electrolysis with a platinum anode is to sweep out sodium and let hydrogen take its place. The IR spectrum, before and after electrolysis, suggests that hydrogen was present before and after. A rise in one peak of optical absorption (3620 cm^{-1}) corresponds with a loss of one peak of acoustic absorption (50°K), yet much optical absorption before the electrolysis extends over a far wider range, including at least three peaks shown to be due to hydrogen, viz. 3435 , 3371 , and 3311 cm^{-1} .

When quartz is subjected to various treatments such as (1) high temperature electrolysis with control of the electrodes and ambient atmosphere, (2) high temperature annealing with control of the atmosphere, and (3) irradiation by X-rays or neutrons, the value of Q and its temperature dependence are known to vary, and also the IR absorption. Hence, it appears that profitable correlations of Q and IR absorption can be made.

Haven and Kats⁽¹⁹⁾ demonstrated that the main hydrogen absorption bands or deuterium absorption bands are modified by the presence of impurities.

Since the concentration of hydrogen in quartz can be calculated from the absorption

(19) Haven, Y., Kats, A., *Silicates Industriels*, March, 1962.

(20) Wood, D., J. Phys. Chem. Solids, 13, 326-336 (1960).

band, it seems probable that not only can certain impurities be identified, but their amount can be determined from the peaks found near the specific hydrogen bands⁽¹⁷⁾.

4.3 Measurement of Q of Precision Resonators

4.3.1 Techniques

The methods of measurement of 5 Mc precision resonators (Type BG61A-5) have been improved steadily through the life of this contract. The purchase by the Electronic Research Division of a Rohde and Schwarz Frequency Synthesizer greatly improved and simplified resonant frequency measurements. After initial measurements on resonators in evacuated envelopes demonstrated the sluggishness of response to temperature change (making Q vs temperature runs extremely tedious), the later resonators from Bliley Electric Company were ordered filled with 1 mm Hg pressure of He. Temperature control was improved further by replacing the copper isothermal enclosure with a Pyrex test tube, insulating the specimens from the violent temperature changes normally encountered near the liquid-gas interface in the dewar flask. These changes made possible the completion of a measurement run over the range -196°C to about 25°C in four or five hours instead of the previously necessary eight hours.

The technique of measuring mechanical quality factor Q was the transmission method. The Frequency Synthesizer was adjusted to 50 mv for each measurement. The leads to the specimen resonator were double shielded. Current through the resonator was measured with a Bruel and Kjaer heterodyne frequency meter, across 10 ohms for the resonant frequency, and across 10^5 ohms for the antiresonant frequency. The temperature was measured with a thermocouple adjacent to the glass envelope of the resonator.

The electromechanical coupling factor and the dielectric constant of quartz change very little over the temperature range used here. Never-

theless, the frequencies of minimum and maximum impedance (related to the coupling) were measured for each point. A single capacitance-vs-temperature run was made on a separate AT-cut crystal of reasonably high capacity, showing that the capacity did indeed remain constant. Q was calculated from the usual relation:

$$Q^{-1} = 4 \pi \Delta f C^T R_R . \quad (1)$$

R_R was determined by substituting a set of resistors for the specimen and plotting voltmeter readings vs resistance. During a temperature run the characteristics of the cables were assumed to remain constant, and the voltmeter readings were converted to resonant resistance from the calibration plot.

To prove the method, a few admittance-frequency runs were made over the resonance, measuring the width of the resonance at a specific fraction of the peak current and determining Q from the amount of fractional detuning:

$$Q^{-1} = \frac{(\Delta f \text{ at } 0.707 i_{\text{peak}})}{f_R} . \quad (2)$$

The two methods were found to agree within the limits of error of each when the calibration plot was used to correct for the reactive properties of the cables.

The self-consistency of the measurements involved in the substitution method (Eq. 1) was checked by repeating the set 10 times at room temperature. Overall deviation was about $\pm 5\%$, almost entirely due to the resonant resistance measurement.

The temperature was varied by moving the resonator in or out of the large test tube inserted in a dewar about half-full of liquid nitrogen. Coarse changes were made by shifting ring-stand clamps, and a vernier screw could be used to make fine temperature adjustments.

4.3.2 Results

The results of measurements made on resonators in evacuated envelopes are repeated in Figs. 34 and 35 (Figs. 9 and 10 of Ref. 21). These include Q^{-1} vs temperature runs on two resonators each of SARP 4-17, SARP 4-23, and Clevite 54F-4; and one natural quartz resonator.

The improved techniques mentioned in the previous section allow more detail in the curves in regions of rapidly changing Q . It is easier to spot spurious or double resonances. These spurious resonances almost always degrade Q of the main mode, and, if strong, appreciably change the frequency-temperature characteristics. A majority of the resonators measured showed spurious resonances at one point or another in the temperature range covered, presumably not due to loss mechanisms inherent in the quartz itself. Therefore, where spurious resonances were detected, these spurious "loss peaks" on the Q^{-1} vs temperature curve were by-passed with a dotted line. Thus Fig. 36 has been modified by the frequency information of Fig. 37, removing one of the loss peaks.

Figure 36 is the Q^{-1} vs temperature curve for a resonator of 54F-4 in a helium-filled envelope. Comparing this curve with those from 54F-4 shown in Fig. 35 discloses two discrepancies. One is the loss peak in the former at -110°C . The other is the increasing loss of the latter as liquid nitrogen temperatures are approached. The presence or absence of part of the seed veil, or of the optical discontinuity caused by the temperature dip may explain those discrepancies. See Table II and note, p. 38.

Figures 38 and 39 show similar Q^{-1} vs temperature curves for two SARP crystal growth runs: 5-38 and 7-19. These have better Q 's at room temperature, but show the characteristically increasing loss at the lower temperatures found also in SARP 4-17 (See Fig. 34).

(21) Hale, D. R., Carlson, A., Krueger, H., Contract DA-36-039-SC-87372, Third Quarterly Report, September, 1962.

FIGURE 34.

Q^{-1} VS. TEMPERATURE
5 Mc PRECISION RESONATORS, TYPE BG61A-5

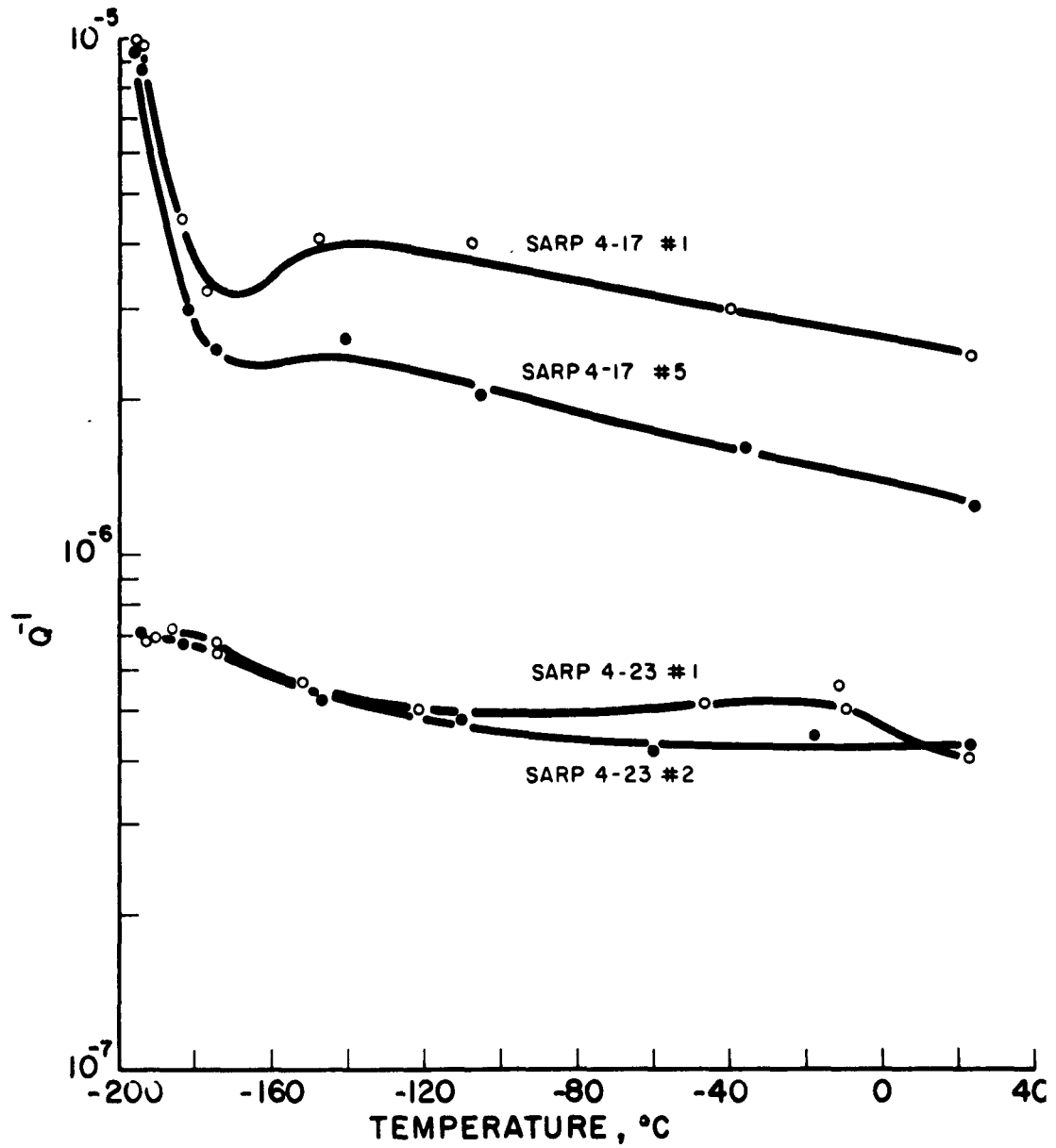


FIGURE 35 .

Q^{-1} VS. TEMPERATURE
5 Mc PRECISION RESONATORS TYPE BG61A-5

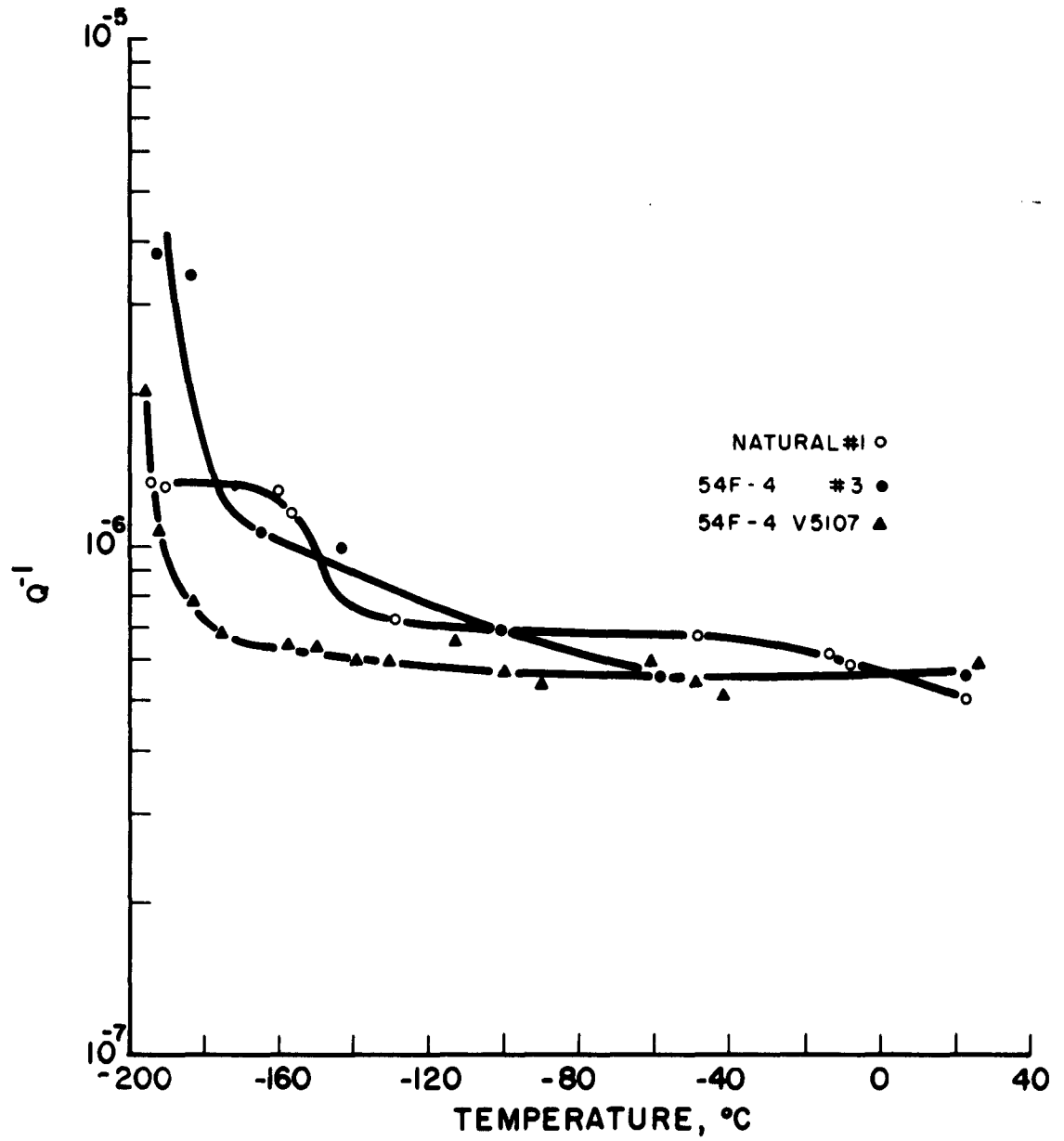


FIGURE 36.
Q⁻¹ VS. TEMPERATURE
54 F-4 V 5194 A

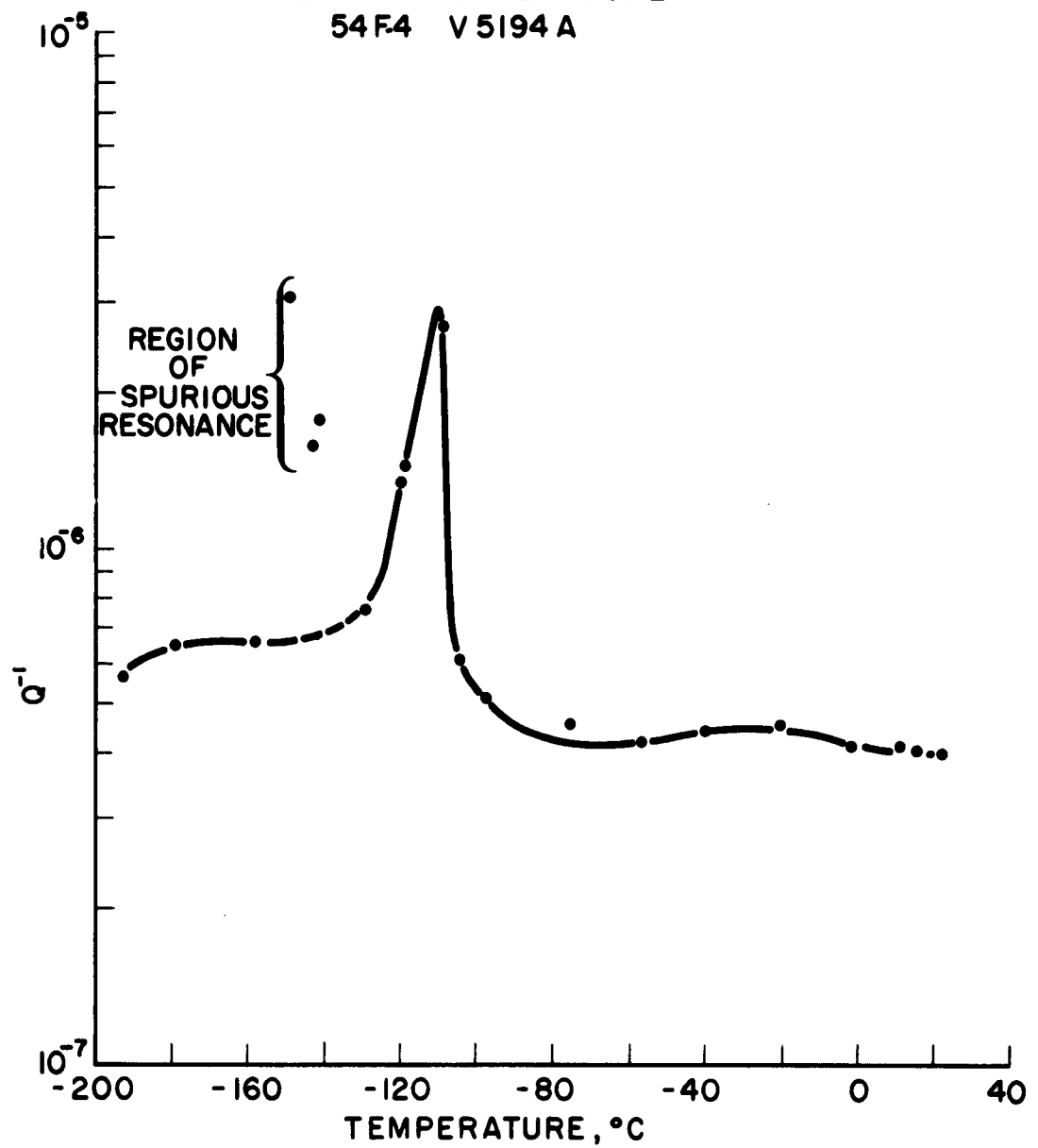


FIGURE 37.
RESONANT FREQUENCIES VS. TEMPERATURE.
54F-4 V5194 A

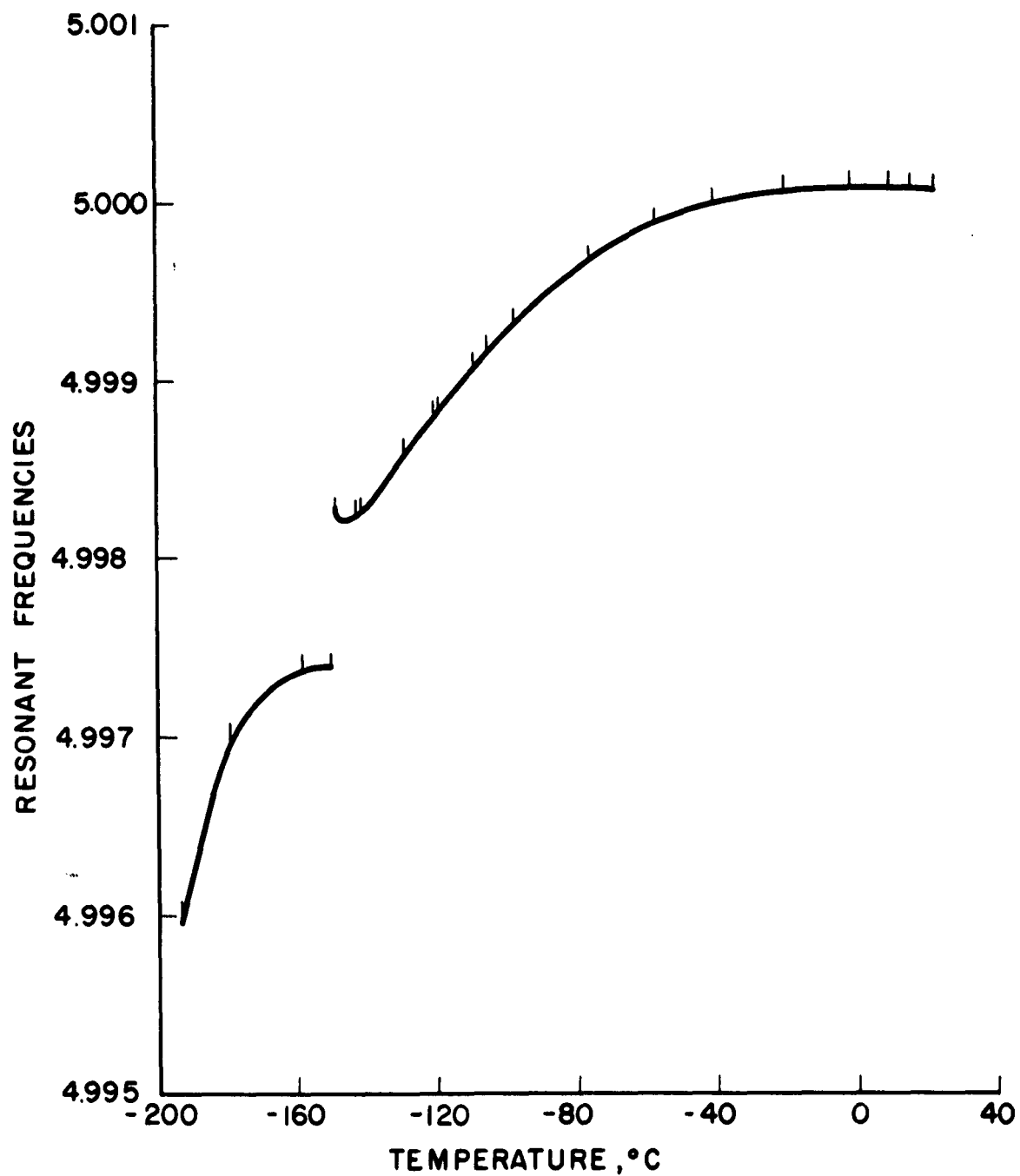


FIGURE 38.
 Q^{-1} VS. TEMPERATURE
SARP (5-38) 637 A

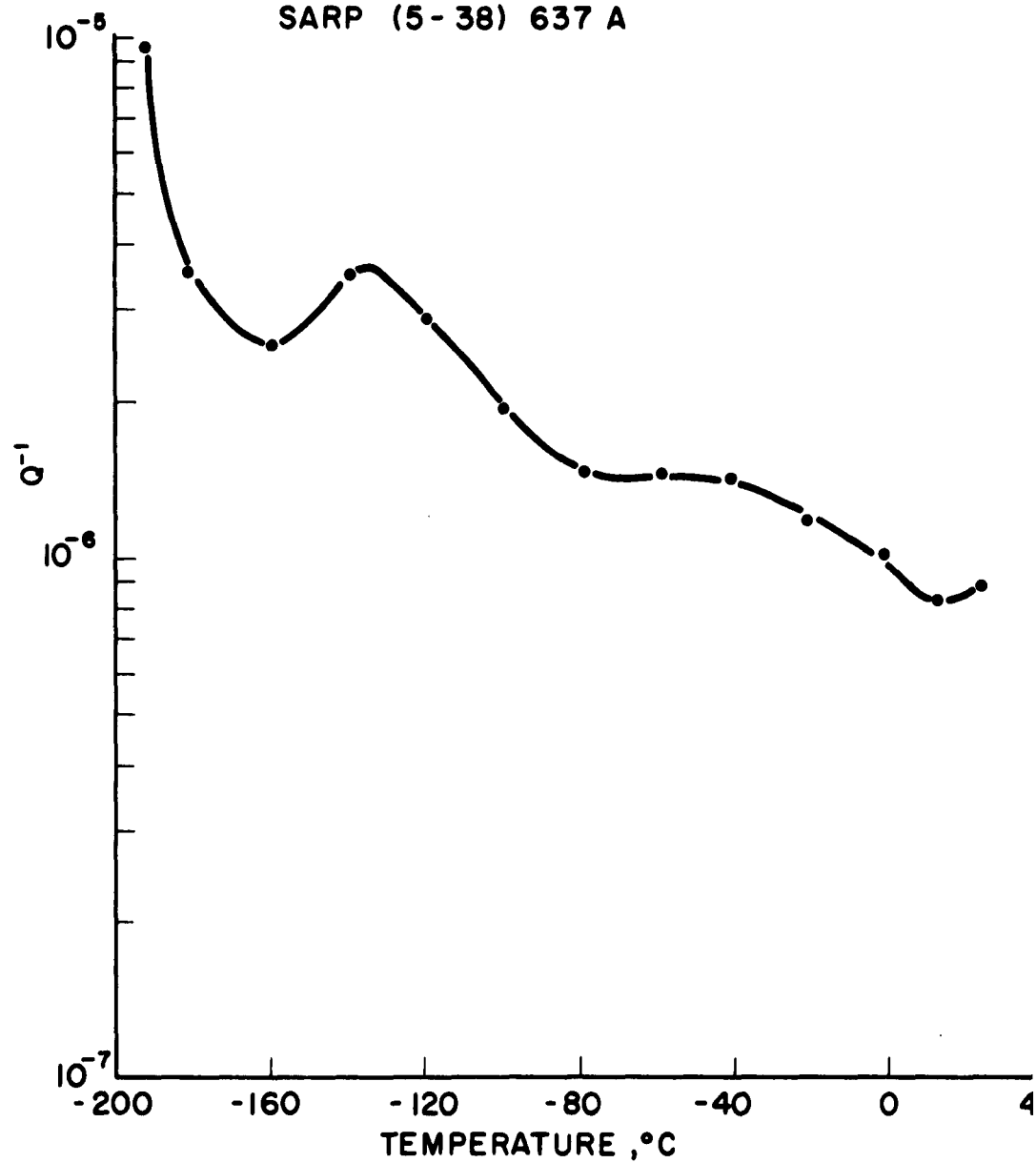
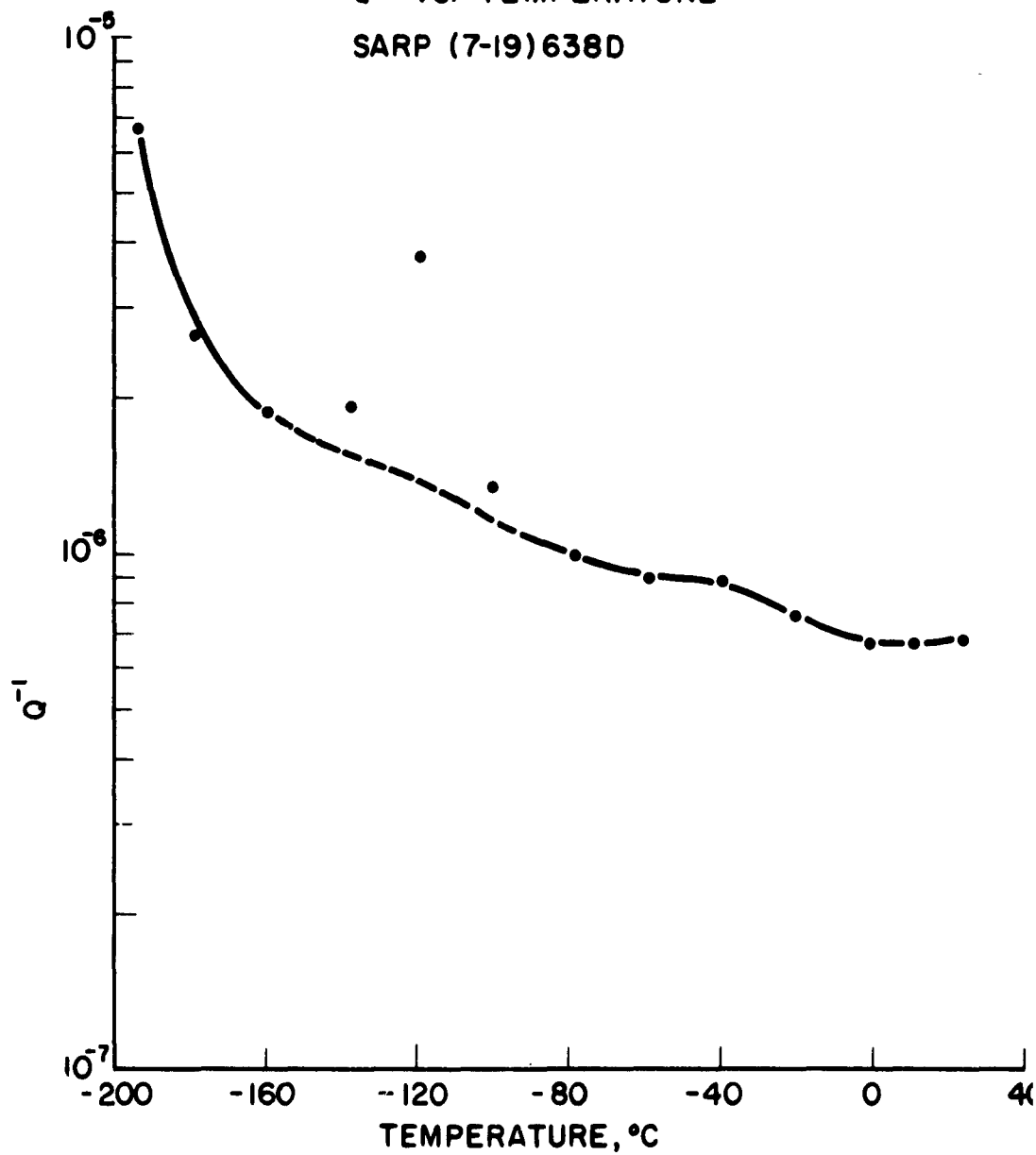


FIGURE 39.
 Q^{-1} VS. TEMPERATURE
SARP (7-19) 638D



The curve for the slow grown Clevite 43B-4 (Fig. 40) shows a vestige of the -110°C loss peak mentioned above for the 54F-4, and another peak very likely caused by proximity to a spurious resonance. No spurious resonances were found, but some anomaly is indicated in the frequency-temperature curve between -140°C and -160°C .

The resonator made from Western Electric Company synthetic quartz shows low Q over the entire temperature range (see Fig. 41). It may be recalled that the loss for the WE 23-13 was satisfactorily low over this temperature range for 100 Mc resonators. (See Fig. 4 of Ref. 2). It was concluded at that time that the 100 Mc resonators could not differentiate between good and excellent synthetic quartz.

4.4 Quartz Crystal Growth

4.4.1 Hydrothermal Experimental Growth

The quartz crystals were grown in steel pressure vessels, details of which are given in Section 4.4.4, Equipment. The vessels hold the growing-system as a vertical cylinder heated at the bottom, cooled by radiation at the top. Silica nutrient material is placed in the bottom; seeds and holding gear are placed in the upper part, and the remainder of the internal volume is filled completely - at operating temperature - with alkaline solution.

Seeds for the current contract were mostly Z-cut plates, with occasionally an X-cut or a minor-r plate added. The Z-cut plates were from synthetic Z-growth, including in some instances, swept Z-growth furnished by Sawyer Research Products, Inc.

Part of the plan was to grow on pre-examined Z-plates as seed, so that comparisons of grown quartz with defects characterizing the seed could be made. Fourteen such plates were prepared, examined optically, and used in about six runs. Several of these involved the new nutrients and such Z-seeds

FIGURE 40 .
 Q^{-1} VS. TEMPERATURE
RUN 43B-4 636 A

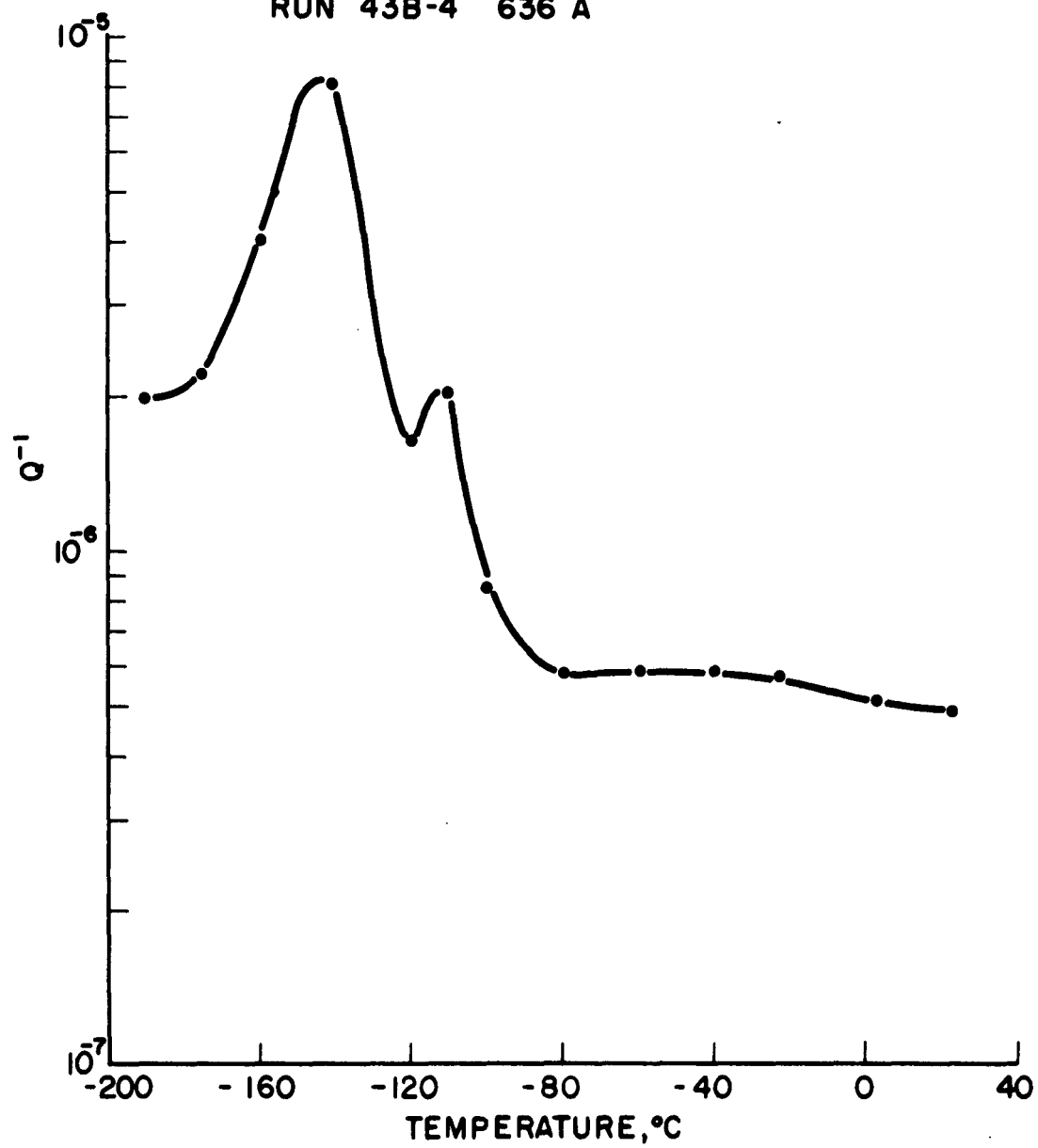
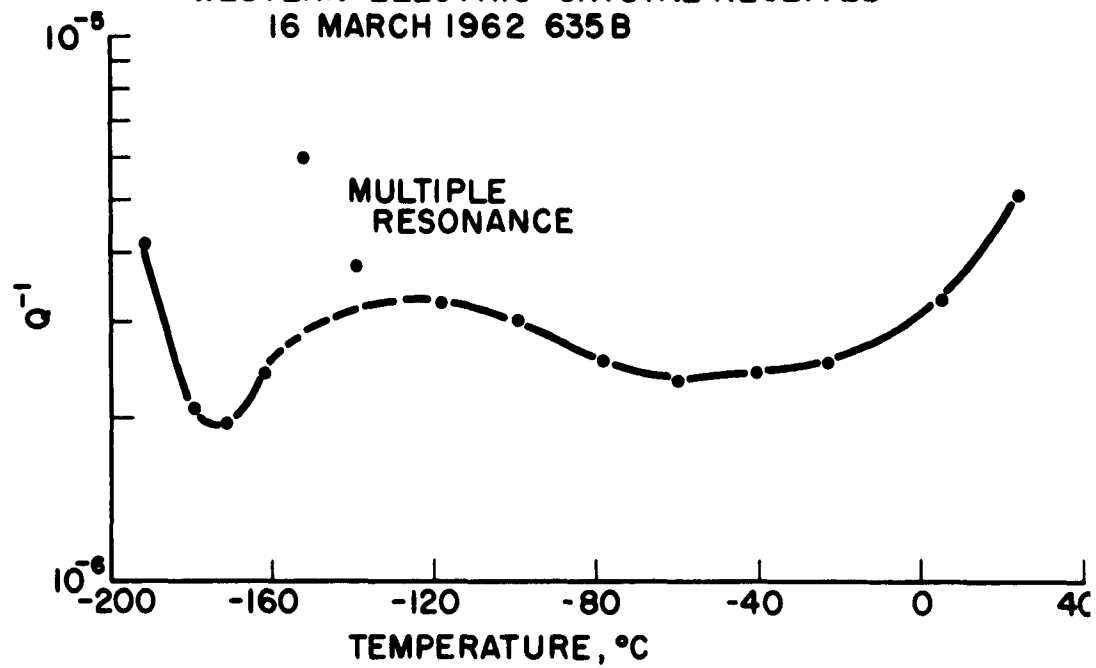


FIGURE 41.
 Q^{-1} VS. TEMPERATURE
WESTERN ELECTRIC CRYSTAL RECEIVED
16 MARCH 1962 635 B



as were used were embedded in creviced Z-growth which then could not be examined. Subsequent experiments and examinations have shown that X-ray diffraction studies would be preferable to optical and would indeed be very useful for a study of the lineage of defects from a parent seed.

Seed holders were in general vertical frames made of stainless steel provided with two small vertical ridges confining the edge of the seed plate. The steel plates were further covered with .005 in. fine silver to prevent the grown material from clinging to the holder.

Nutrient consisted of chunk Brazilian quartz, pieces of Z-growth synthetic material, pieces of devitrified Corning 100% silica, small slabs of L. Light Co. Lump Silica, or pieces of devitrified silica gel. The materials are identified in the Table I.

Seeds and nutrient quartz or vitreous silica were cleaned an hour in 1:1 HCl, a quarter-hour in 48% HF for 100 g charges of nutrient. For the charges of about 400 g the nutrient cleaning was lengthened four-fold.

Solutions were all 0.83 molar with respect to sodium carbonate, J. T. Baker Chemical Company, Lot 20023. Solution preparation is further discussed in Ref. 3.

The upper end temperature is controlled by the character and thickness of the thermal insulation applied to the vessel. The obtaining of small temperature differences (when desired) has been the subject of much study and discussion, and is by no means settled. The few experiences with heaters at the top as well as at the bottom have given cooler regions between. Bottom heat and insulation are therefore the standard means of heating and obtaining temperature difference. Recently an improved control of low temperature difference was attained by arranging an air space of about 3/4 in. around the vessel from bottom to top, and outside of this space placing six inches of Kaylo and glass-wool insulation. Care is taken also to see that the heated air has no easy way out of the insulation. Under Run 54E-6 the insulation is further discussed.

TABLE I. CRYSTAL GROWING RUNS MADE DURING CONTRACT PERIOD

Run	Date Closed	Duration (days)	Nutrient	Degree Fill (°C)	Temp. Cryst. (°C)	Temp. Diff. (°C)	Press. (kpsi)	Growth Rate $\frac{\mu\text{Z}}{\text{mm/day}}$	Location Original Discussion	Chemical Compos. Obtained	Defect Study Optical X-ray
44B-19	16 Sept 1962	49	B	.70	353	35	6e	.21	Report #7		
44C-26	19 Sept 1962	94	Z	.70	330	42	3e	.36	#7		
44E-32	24 Aug "	51	Z	.70	358	30	5e	.53	#7	*	
44F-7	19 Oct "	108	Z	.70	355	32	7.8e	.11			
50C-18	24 Apr. "	46	G-3	.73	320	50	5.2e	(r.45)	#5		
50E-6	19 Nov. "	55	Spec.	.70	351	32	4e	.33			
50F-6	2 Oct. "	68	Z	.70	362	24	6.5e	.5	#7		
50J-3	14 May "	32	C	.68	381	34	9e	.77	#5, #6		
50J-4	29 Oct "	120	C	.70	318	14	3e	.14	*		
50K-2	14 May "	32	C	.70	384	24	6.5e	.47	#5, #6		
50K-3	21 Sept "	85	Z	.70	356	34	6.5e	.29	#7		*
50K-4	31 Jan. 1963	50	L	.70	353	17	3.5e	.11			
54A-9	6 Sept 1962	34	G	.83	312	6	1.9	.15	#7		
54B-8	24 Aug 1962	125	C	.83	308	30	4.9	.15	#7		
54C-7	7 Sept 1962	99	C	.80	310	34	6.4	.10	#7		*
54D-7	2 Jan 1963	172	C	.70	350	32	7.7	.15			
54E-6	2 Jan 1963	232	B	.81	313	15	7.5	.08			
54F-5	23 July 1962	89	C	.81	304	22	2.2	.23	#7		
54F-6	2 Jan 1963	113	Z	.70	333	36	2.2	.11			

Nutrient: B, Brazil lascar

Z, Z-growth

G, Gel from Ethyl Sillicate (G-3, gel from undistilled E.S., 300 ml, plus 60 ml 1% HCl).

Spec. Special, Z-Growth from Run 54B-8

C, Corning #7940

L, "Lump Silica" from L.Light & Co.

Pressure: e, Estimate from filling-temperature data.

In all runs lasting over two weeks, the thickness of crystals was monitored by means of gammagraphs which were taken with a cobalt-60 source of about 250 millicuries, and Kodak "No Screen" Medical X-ray film. The film is placed about 8" behind the autoclave and the source distance is varied depending on the exposure time and the thickness of the autoclave. By knowing the inside diameter of the autoclave the crystal thickness may be calculated by using the proportion:

$$\text{Crystal thickness} = \text{Crystal thickness on graph} \frac{\text{I. D. on graph}}{\text{Actual I. D.}}$$

Estimates made using this method are accurate within about 1 mm. The source is used, and personnel are protected, under the Title 10 Regulations of the U. S. Atomic Energy Commission.

Difficulties encountered in the crystal growing include the following: occasional failure in temperature control equipment and at least two failures of electric power supply; pressure losses through vessel seals; nutrient showing growth on upper portions, even to a bridging over the diameter of the vessel; temperature differences (the control of supersaturation) rising to undesirable values, yielding crystal nucleation on upper walls and creviced growth.

4.4.2 Growth Runs and Discussion

Nineteen successful experimental growing runs were made, summing to a total of 1554 growing days. (Table I).

Most of these experiments have been discussed in Quarterly Technical Reports and reference thereto is made in the accompanying table. However, the following general discussion of individual runs will draw on and amplify the earlier discussions. The order of listing is by experimental run and is therefore not chronological.

RUN 44C-26.

This run was one of four to examine the addition of pentavalent phosphorus to quartz. (Refer to Sec. 4.4.5 on Phosphorus Additive). One run failed through leakage. Seeds were Z, X and minor-r. A power failure after 33 days produced 2 veils of inclusions easily seen in the Z-crystal. This Z-crystal grew into the wall and shows liquid-vapor inclusions; nevertheless, part of it may be suitable for making a small precision resonator. The other crystals are of good quality.

A simple examination of the crystals indicates nothing about the effect of the additive on the crystal. The crystals will be made available for Signal Corps observation and study.

RUN 44E-32 (Phosphorus Addition).

The seeds were Z and minor-r; the crystals were all clear, though the Z-crystal was flawed. The temperature controller cycled over a few degrees, a trouble that did not respond to attempts to adjust it. The top chunk of nutrient bridged across chamber and grew. The observations point to too much oversaturation. Spectrographic analysis disclosed that the aluminum content is unusually low.

RUN 44F-7 (Phosphorus Addition).

This run produced clear growth on a minor-r crystal, fair growth on an X-crystal, and fissured growth on the Z-crystal. The minor-r crystal which grew so far that the minor-r faces are missing, was irradiated with 50 kv x-rays and showed considerable darkening in the minor-r growth. The depth penetration of the darkening is uncertain.

RUN 50C-18 Silica gel was employed, with 10 days at about 211° in a devitrifying cycle. Walls were thinly crusted and 16 g. of crusty material (microcrystalline) were taken from the vessel. The minor-r grown crystals were cracked. They grew at about 0.5 mm/day, rather fast for this size of vessel. Excess supersaturation is blamed for the flawed growth, as is discussed under Sec. 4.4.6. Devitrification Process Examined, p.43. A slice of crystal was prepared for determining chemical composition and effect of radiation. The solution was yellowish, suggesting that the organic compound yielded the coloring material.

RUN 50E-6. High visual quality quartz was grown using as a nutrient the cracked Z-growth produced in Run 54B-8. In this earlier run, use was made of Corning nutrient and in spite of care in devitrifying the material and in attempting to secure a low supersaturation, the Z-growth quartz was seriously damaged by crevices. It is believed, as discussed, in Section 4.4.6 that the damage is due to too-high supersaturation during the growth run because of the high dissolution

rate of the devitrified nutrient. The creviced crystals from 54B-8 were cooked in 10% NaOH to remove a white deposit of amorphous silica. The bars were broken into approximately 15 g pieces. Z- and minor-r seeds were used. The product of this run (50E-6) was two crystals of excellent visual quality, a fact which confirms the suspicion that the poor growth in 54B-8 was due not to the composition of the nutrient, but due to its high dissolution rate.

A spectrographic analysis of this material would be interesting to show whether in fact the grown crystals were reasonably pure.

RUN 50F-6

Use was made of a special solution with D₂O to make the 0.83 molar Na₂CO₃. Z-growth chunk quartz was the nutrient. Z, X, and minor-r seeds were represented. The autoclave was silver-lined although the lining was broken near the top, exposing steel. Gammagraphs were taken at 21 and at about 66 days at which latter time the Z-crystal showed occupation of the vessel diameter. The crystal was impossible to dislodge even after attempts to dissolve away the edges with HF. The X and minor-r crystals were clear though cracked.

RUN 50J-4

This run in a platinum-lined vessel had Corning silica as ultra pure nutrient. The chunks of nutrient were chosen to be 1 to 1.3 cm across. Devitrification was effected at 30% fill, 450°, 5-1/2 days. A low temperature difference was desired, and the 14°C was considered very acceptable; it was hoped, therefore, that the rate might be sufficiently low to yield clear growth. The solution was the specially prepared and filtered 0.83 sodium carbonate. (Ref. 3, p 13). A special polished, etched, and examined Z-seed was used. The run was followed by gammagraphs and closed when the Z-crystals seemed to come fairly close to the side of the vessel. All three crystals, two Z-crystals and a minor-r crystal, contained solid inclusions and are cloudy and cracked. The Z-crystals took on a light yellow coloring, and were found to contain platinum, and to have an exceptionally low aluminum content.

RUN 50K-2

This experiment, again in a platinum-lined vessel, had as nutrient 100 g of Corning vitreous silica which was subjected to devitrification process of seven days at about 260°C and a degree of filling of .40. The experiment preceded the 50J-4 just mentioned, and a milder devitrification cycle was used. In the growing cycle all of the nutrient disappeared, 46 g being transferred to the seeds. The crystals were creviced, showing rhombohedral

faces on many of the jagged points. This was one of the results which led to the employment of a more intense devitrification cycle.

RUN 50K-3

The run (in platinum) was designed to yield visually clear material. Lascas nutrient was used in view of the troubles had with the untrapure amorphous silica. The amount of nutrient was increased to 150 g to allow growth of larger crystals. Difficulty with the Fenwal thermoswitch produced a large overshoot in temperature, which, with the cooling to check on whether the vessel had leaked, may have deposited spontaneous nuclei and started creviced growth. Some of the material of the Z-crystal is colored yellow. Observations lead to the conclusions that visually clear, electronic grade quartz can be had from this autoclave.

RUN 50K-4

Lump silica of ultra purity from L. Light & Company, England, was used as nutrient in this platinum-lined vessel run. Two slabs of the material were placed in the bottom of the vessel. The exposed area of the combination was about 40 cm², a low value compared to the usual surface area of a comparable weight (73g) in chunks of lascas, etc. The devitrification stage was 30% fill, 450°C, 5 days, at the end of which time the solution had disappeared and the nutrient looked white instead of the original yellowish.

The deposited quartz on a Z-seed and on a minor-r seed, contains much that is visually of high quality. However, there is a veil on the seed seemingly consisting of microscopic bubbles (so small they do not show as liquid-vapor inclusions under 36 magnification). Also there are a few solid inclusions. An outstanding feature of Z-growth is that it is not creviced as is most of that grown from amorphous nutrient. This process improvement may well have been due to the reduced area of the nutrient.

The residual nutrient was in the form of a shell of small quartz crystals, the walls consisting of parallel drusy growth with caps pointed inward (a result consistent with other observations on vitreous nutrient).

RUN 54C-7

The main variables were similar to Run 54F-4 except for use of Corning silica nutrient and higher temperature difference. Vitrification cycle: filling 0.40, temperature 250°C, time 7 days. Recorded average temperature 240°C, pressure 250 psi for the process. A sample of nutrient was examined by the crystallographic laboratory, and amorphous material was found in it possibly to the extent of 9%.

At the start of the growing cycle the 10,000 psi rupture disk let go. Either the calculated .80 degree of filling was accidentally surpassed or the rupture disk had become weak after several runs. The available volume was now

awkward to measure with the network of caves in the nutrient. A volume of solution almost sure to be in excess was therefore used, and as the pressure rose above 6500 psi on the heating up, the excess was bled off through a valve.

In this Run, smaller Z-seeds were cracked, though not creviced, and the two minor-r crystals were of good visual growth.

RUN 54D-7

This long run using a Corning nutrient and a reasonably low temperature difference of 32° (although a still lower temperature difference was desired and was attempted) yielded some of the most nearly visually perfect growth so far obtainable from this nutrient. In attempting to secure better control of the growth the supply was held in a wire cloth basket provided on the top with a funnel-type baffle. The basket was not removable undamaged. Use of basket and baffle did yield, however, an improvement in quartz growth from vitreous material.

The Z growth is not nearly so creviced; on the contrary it shows the cobblestone effect with indications of spiral dislocations on many of the mounds. However, on rhombohedral faces of the Z-growth crystals there is often evidence of small areas of twinning. These Z-growth crystals are cracked. A crystal grown on an X-cut strangely shows nearly equal growth on the two sides. The growth is not cracked as is so evident in the minor-r crystal, but the growth includes liquid vapor inclusions and also a large scattering of very fine solid inclusions.

RUN 54E-6

This run using lascas nutrient and a low temperature difference of 15° was the longest of the contract. The growth was followed by gammagraphs, providing evidence of the low growth rate and indicating when the run should be ended. The growth quality of the Z-crystals seems very high. On the minor-r crystals, of which there are three, the growth was unusually slight. Thus on the Z-seeds the growth was about .08 mm/day, whereas on the minor-r seeds, .002 mm/day.

A special arrangement of thermal insulation is believed to account for the desirably low temperature difference: the vessel was heated partly by two 100-watt heaters strapped close to the bottom. A cylinder of Kaylo insulation 1-inch thick enclosed the vessel, reaching half a foot above the top. This cylinder hugged the screw cap of the autoclave and left an air space of about 1 inch along the chamber of the vessel including the length occupied by the heaters. During this run at the 94th day there was a power failure of 28 minutes during which the temperature dropped about 15°. Thus there should be in this run the type of discontinuity notice in the crystals from Run 54 F-4. See the discussion of x-ray diffraction pictures for Run 54F-4, Section 4.2.2.2.

RUN 54F-5 The nutrient here was Corning silica devitrified during about 10 days at 0.40 filling and about 250°C. Difficulties were encountered in the experiment, the temperature difference running higher than expected for some days (72°C) and the pressure remaining low. The growth was in general flawed.

RUN 54F-6 This run was a study of the effect of lithium and fluoride as additives. The solution was made up to yield a molarity of 0.058 LiF in the solution. The three Z-crystals grew well with the cobbles on the surfaces tending to be large. Total growth was a maximum of 14 mm hence too small for making 5 Mc precision resonators. X and minor-r seeds were also grown, and came out well.

Notes on earlier Runs (Table II) which provided crystals for X-ray or resonator measurements:

RUN 50A-7 This run made use of conditions shown earlier to yield no heavy phase (this phenomenon discussed in Ref. 22). Utility: to determine whether circulation conditions around nutrient might be improved, whether residual nutrient could not be removed more easily. Growth quality was excellent, there was no evidence of heavy phase. The conditions, therefore, are considered excellent.

RUN 42B-13 Utilizing a higher degree of filling than normal (0.77) and a lower temperature (335°C) the growth run yielded approximately 320 g. of visually high quality Z-growth. The run was closed by failure of an over-heat relay at end of 60 days, and was followed up with Run 42B-14 - also very successful. Noteworthy in this Run 42B-13 was Z-seed #6 which had been grooved in X-direction with saw cuts and diamond scratches. Results of this were described in Ref. 8, pp. 27, 28, Fig. 10. (Page 26, this Report).

RUN 54F-4 Noteworthy in this run were several failures in electric power that resulted in noticeable temperature dips during the experiment.

Days After Start of Run	Temperature Dip
105	7°C
152	31°C
155	10°C

Optical discontinuities, particularly at 152 days, were noticeable in the grown crystal and again in the X-ray exam-

(22)

Jost, J. M., First Quarterly Report, 3C-65589, May, 1955, p. 25-29.

TABLE II. QUARTZ SPECIMENS INVESTIGATED UNDER THE CONTRACT, GROWN EARLIER

Run	Date Received	Duration (days)	Nutrient	Solution	Degree Fill	Temp. Cryst. (°C)	Temp. Diff. (°C)	Press. (kpsi)	Growth Rate (mm/day)	Reference
42B-10	June 1957	78	B	.83C	.73	364	13	7.7	0.19	Sc-72415, 4 Qtly June 1957, p. 5.
42B-13	May 1958	60	B	.83C	.77	334	8	9.0	0.15	Sc-72415, Final 1958, p. 27
43B-4	December 1955	160	B	1M Na ₂ CO ₃ .96M NaHCO ₃	.725	299	7	1.5	0.14	Sc-64589, Final 1956, p.6,19
44E-13	December 1956	55	B	.83C .008M NaAlO ₂	.70	345	64	-	0.34	Sc-72415, 3rd Qtly March, 1957, p.4.
50A-7	January 1959	21	B	1.13M Na ₂ CO ₃ +.25M NaHCO ₃	.70	350	30	4.0	0.1	Sc-78247, Final 1959, p. 14.
50J-1	June 1961	21	B	.83C	.70	378	20	6.5e	0.24	Sc-87372, Final, 1961, p.5,12,28
50K-1	October 1961	118	Zs	.83C	.70	430	20	13.5e creviced		Sc-87372, Final 1961, p.3,6,15
54C-6	January 1960	243	S	.83C	.75	369	25	8.4	0.2 est	Sc-87372, 1st Qtly, Jan.1961,p.3
54F-4	October 1961	224	B	.83C	.81	314	14	5.8	0.10	Sc-87372, Final 1961, p. 10

TABLE II. QUARTZ SPECIMENS INVESTIGATED UNDER THE CONTRACT, GROWN EARLIER

Run	Date Received	Duration (days)	Nutrient Solution	Degree Fill	Temp. Cryst. (°C)	Temp. Diff. (°C)	Press. (kpsi)	Growth Rate Z (mm/day)	Baffle, % Open	Vessel ID
SARP 1-31302	May, 1961	40	B	.83C	.80	355	9 av 11-13	.8 to 1.0	?	8"
4-17	?	40	B	.83C	.79	355	6.5 av 11	.83	20%	8"
4-23	(Resonator only)	60	B	.83C	.79	355	5.2 av 11.9	.58	30%	8"
5-17	Mar., 1962	20	B	.83C	.76	355	10.5 av 12.8	.74	7.5%	8"
5-38	"	30	B	.83C	.76	355	19.3 av 11.7	.92	7.5%	8"
7-19	"	40	B	.83C	.76	354	11.0 12.2	.74	8.5%	10"
WE 23-13* Jan., 1961										
WE 16	16 March 1962		1M NaOH	-	between 343° and 400°C		- 23	2.0		
<hr/>										
Nutrient:	B, Brazil lascas; C, Corning #7940 Zs, Swept Z-growth; S, Special, Z-growth from Run 42B-12		SARP, - WE, - *WE 23-13						Sawyer Research Products, Inc. Western Electric Company	
Vessels:	50J, 50K are platinum-lined.								Received January 1961, is believed to have been grown under essentially the same conditions as the crystal received later.	
Growth Rate is for both sides together.										
Solution:	83C is 0.83 molar aqueous sodium carbonate									
Pressure:	e, estimated from filling-temperature data									
Temp. Diff.	If av, the variation was about +2°.									

inations (pp. 19, 20, 21, this Report).

Bliley Electric Company, while fabricating the Quartz 54F-4 into 5 Mc resonators, noted a bluish line and rows of "bubbles" in the blanks. The line is believed to be the refractive index discontinuity caused by the largest temperature dip during the run, and the "bubbles" are believed to be seed-veil particles. The Z-growth of the crystal being a little short of adequate, the AT-resonator blanks were cut at the request of Clevite with the edge partly into the seed. It is noteworthy that these nonuniformities did not prevent Bliley from preparing high Q units.

4.4.3 Chemical Compositions

Chemical compositions by spectrographic analysis are shown in TABLE III for several crystals grown under the current contract and for other quartz material studied.

Platinum was found in the yellowish material grown in RUN 50J-4, a platinum-lined vessel. A standard for platinum not being available, the content of the metal can only be estimated as about 300 ppm. The sample examined was cut from the most yellow part of the Z-growth crystal. The presence of the platinum was entirely unexpected. Its ionic radius of 0.55 \AA explains that it can enter the lattice if available in the solution as an ion. Hypothetically it can be assumed that platinum occupies silicon sites. As in the case of 4-valent germanium, minor-r growth may darken with X-irradiation.

The low Al content of synthetic quartz has been actively pursued, especially in RUN 50J-4 which grew quartz from an ultra pure nutrient inside a platinum membrane. The nutrient was not analyzed; it is believed to have an aluminum content of from 90 to 330 mg per g quartz. It is noted that, had the autoclave and its charge contained no aluminum at all, a single particle of aluminum of diameter about 0.2 mm could account for the ppm found in the quartz. It was part of the plan to continue further experiments by preparing the solution and loading the vessels

TABLE III. SPECTROGRAPHIC ANALYSIS OF SEVERAL QUARTZ SPECIMENS EXAMINED

37-10 42B-10 42B-11 43B-4 44E-13 44E-32 50J-2 50J-4 50K-1 54F-4 SARP SARP SARP WE23-13 WE														Limit of De-		
r	Xf	Z	Z	Z	Z	Z	Z	Z	Z	Z	Z	Z	Z	16 Mar. 1962	tectability.	
Ag				0.30			0.5	0.16		0.18		0.21			.06	
Al	151	60	47	100	143	1.45	6.2	1.9	4.4	17	113	46.8	22-66	175	35	.44
Ca	7.3	14	18	8.9	18						5.8		N.D.	7.6		3.0
Cu	ND	0.7	9.5	5.3	0.5	1.5	2.8	1.1	0.94	1.3	6.3	1.0	1.8-6.5	1.0		0.2
Fe	39	76	51	180	12	40.6	30	31	100	33	300	35.6	2-4	170	13	7
Ge					N.D.							N.D.				8
K													15			1500
Li	10	4.3	ND	10.4	5	N.D.		N.D.		16		35	16-40	20	<26	3.4
Mg	10	11	16	9.6	7	0.7	7.4	0.9	7.4	0.5	17.3	0.5	N.D.	163		.25
Na	167	39	105	88	138	20		391		130	109	62.8	26-78	272	86	26
Pb							29									
Tl						7.3		18		N.D.		N.D.	N.D.			

Quartz Growth type indicated

Composition expressed as atoms impurity per 10^6 atoms silicon

Accuracy $\pm 10\%$ except as indicated $\times/3$

Blank space means not looked for

For the analytical information on SARP Typical, and on WE 16 March 1962, acknowledgment is made to the supplier.

in the available clean room. Miscellaneous difficulties - mostly mechanical and incidental - yielded only five runs in the vessels, a total of 319 days operation.

The large iron content was not anticipated, though iron is a likely constituent of laboratory dust.

The extremely low Al-content of the phosphate run, 44E-32 was surprising for its suggestion that possibly the presence of phosphate had an effect of retaining Al in the solution.

Baumbauer⁽²³⁾ and Kats⁽¹⁶⁾ found that the concentration of trivalent ions and of monovalent ions were often substantially equal. These summations are not followed. The concentration of protons can be supposed, at first approximation, to be the same for all four runs, since they all used 0.83 molar sodium carbonate. The summation law not holding, it is uncertain whether to look askance at the analytical data or at the material, which is synthetic; it was data on natural quartz that suggested the rule initially.⁽²³⁾

4.4.4 Equipment

Aside from general laboratory supplies and equipment, the task of growing crystals under the Contract required autoclaves, furnaces, temperature-control and recording devices.

The vessels used in the contract were

AUTOCLAVE No.	ID (in.)	Inside Length (in.)	Volume (ml)	Maximum Working Pressure (psi)	Maximum Working Temperature °C
44	1.5	10.2	285	7000	400
50	1.5	10.2	285	15000	400
54	2.56	21	1780	8000	425

(23) Baumbauer, H. U., Schweiz, Mineral. u Petrog. Mitteilungen, 41, 335 (1961).

The material is 410 high chrome stainless steel. The supplier of Autoclaves of Type 44 and 50 is the High Pressure Equipment Co. of Erie, Pennsylvania. The supplier of Type 54 is the American Instrument Company, Silver Spring, Maryland.

The autoclaves are approved by the Ohio Industrial Commission as "unfired pressure vessels", on the basis of material of construction, dimensions, design of closure. Such vessels are to be fitted with pressure gages and rupture disk assemblies against the sudden rise of excessive internal pressure.

Two Type-50 vessels were lined with platinum by the Baker Platinum Division of Engelhard Industries, Newark, N. J. This required about 12.5 troy ounces of metal each. Obtained on the previous Contract, they required re-conditioning, especially because the sealing surfaces would not separate after a hydrothermal experiment.

One of the vessels as reconditioned maintained a tight seal using the supplied platinum-rhodium gasket and the platinum disk fastened to the cover. On the other, the sealing method described by R. Nacken in 1944 has been entirely satisfactory: .005 in. sheet of platinum laid over the lip of the chamber liner and compressed by the steel surface of the cover. There seemed much advantage in the closure method proposed by the suppliers of the linings, involving a gasket of relatively hard alloy between two platinum surfaces. However, this design has not given satisfaction.

Spontaneous nucleation of quartz in holes through covers of the Type-54 autoclave leading to the gage and other connections caused trouble. The holes are 1/4-in. toward the inside of the vessel, and smaller at the top of the cover where the pressure fittings enter. The nucleation blocked the passage so as to make the rupture disk as well as the pressure gage ineffective. In several of these vessels the holes were opened by diamond drilling, and then partially

closed by plugs of silver rod about 3/8 in. long through which holes had been drilled with a #60 drill. As the vessel is heated at the beginning of a growing run, the alkaline solution, in expanding, passes readily through the hole to actuate the gage. During growing conditions, when the alkaline solution in the autoclave chamber is saturated with silica, the access of silica to the cooler parts of the cover and connections is by diffusion only, and the alkali concentration seems to be ample to maintain it in solution and avoid the formation of the artificial geodes.

Two of the Type-54 autoclaves have been reconditioned at the sealing surface by the machine shop. The sealing surface on the body of the vessel is a narrow shoulder about 1/8 in. wide at the top of the autoclave chamber. In the middle is a groove .010 in. deep into which the softer gasket ring, attached to the cover, is compressed. Compression at the factory - presumably when the vessel is given the hydraulic test - produces a narrow ridge in the gasket ring which fits into the groove in the chamber. It has been found that with ordinary care damage finally results.

4.4.5 Phosphorus Additive

Q of synthetic quartz has been shown to be greatly improved by electrolysis at elevated temperature (Ref. 24, p. 29-36, Ref. 25), and by the addition of lithium to the growth solution⁽²⁶⁾. The assumed mechanism is that aluminum atoms occupying silicon sites in the lattice require charge compensation in the form of monovalent alkali ions or protons. Electrolytic purification has been shown to remove some of the sodium; the addition of lithium to the sodium-alkali solvent may permit this element to enter preferentially to the sodium, perhaps dependent on the smaller size of the lithium ion.

(24) King, J. C., Final Report, Contract DA 36-039-SC-64586, June, 1960.

(25) King, J. C. Proc. Inst. El. Eng. (London), 109, B, (1962).

(26) King, J., Ballman, A., Laudise, R., Phys. Chem. Solids, 32, 1019 (1962).

It has seemed probable that the introduction of pentavalent phosphorus into some of the silicon sites would be a useful, advantageous method of introducing compensatory charges for aluminum impurity and might constitute a hindrance to the inclusion of sodium, of which the growing crystal is always bathed in great quantity.

The ionic radius of P^{-5} at .35 A.u. compares very well with the silicon ion it might occasionally replace: Si^{+4} , .40 A.u., and indeed should be accepted by the quartz structure more readily than the aluminum: Al^{+3} , .51 A.u.

A few earlier experimental growth runs used tri-sodium phosphate to make the alkaline solvent. Well-developed crystals were not produced, however. (27)

Three preliminary growth runs using phosphorus addition were made and reported (Table I and discussion). The resulting crystals were not large enough for the fabrication of 5 Mc resonators. Spectrographic analysis of one crystal revealed a surprisingly low content of aluminum (Table III), which must tentatively be assumed the result of the phosphate addition. No data is available on the content of phosphorus.

(27)

Hale, D., Eighth Quarterly Report, Contract DA 36-039-sc-15381,
August, 1953, p. 15.

4.4.6 Devitrification Process Examined

In order to obtain quartz of ultrapure composition special nutrients were suggested such as semiconductor grade silicon, Corning 100% silica, and gel from ethyl silicate. Semiconductor silicon was studied and reported in Ref. 8, pages 29 and 30. It was shown there that small well-shaped crystals of quartz could be obtained, and reference was made to the Bell Telephone Laboratories study of the hydrothermal method for analysis of traces of boron.

Corning material and ethyl silicate were studied more extensively under the current contract. At first the devitrification cycle was set as follows: degree of filling, 0.4; temperature, 260°C ; sodium carbonate solution, 0.8 molar; time, 7 days. This cycle, of course, did not include the seeds. The degree of filling was made very low to avoid deposition of crystal nuclei on the upper walls of the vessel. A study of the thus devitrified Corning silica by Mr. William Cook showed that the material had become at least 90% quartz. A few experiments with this devitrified material yielded badly creviced Z-growth. Hence, it was questioned whether devitrification had been sufficiently thorough and therefore a more intense cycle was used: degree of filling, 0.4; temperature, 350°C ; time, 3 or 4 days. The estimated pressure in this instance was 2000 psi. Visual examination of this material showed no difference, however, from the material devitrified by the earlier cycle.

An experiment with material devitrified by the earlier method indicated differences in the rate of dissolution: Approximately equal-area pieces of lascas, Corning silica, and devitrified Corning silica were cooked in two molar NaOH at 80°C about 12 hours. They showed the following weight losses: lascas 0.09%; Corning vitreous silica 0.28%; devitrified Corning 8.2%. The extraordinary difference is assumed to be due to the porosity in the devitrified material which is composed of microscopic crystals presenting a very rough surface compared to the pieces of either of the other materials.

Theoretically this fact should cause no great difficulty since it indicates merely that the temperature difference should be made quite small in order to maintain a reasonably small supersaturation. However, the temperatures of the two ends of small laboratory autoclaves cannot be controlled with the amount of accuracy that is desirable.

4.4.7 Growth on Strained Seeds

A number of subordinate projects were merely brushed, and left in an incomplete state. Four of these were (1) purification of sodium carbonate by recrystallization, (2) crystal and specimen plate etching by hot alkaline solution under pressure, (3) growing quartz in excess hydrogen or oxygen, (4) growing on strained seeds.

Regarding (1): In the attempt to produce ultra purity quartz, attention was paid to the vessel walls and all components (nutrient, water, alkali) for the amount of impurities they could contribute. The possibility of securing ultra pure sodium or producing it, and converting to carbonate was considered. The possibility of zone refining sodium hydroxide was considered. Recrystallization of sodium carbonate was chosen as worth a try.

Regarding (2): Hot alkaline etch and HF etch experiments have been frequently made and correlations sought. The density of dislocations as equated to the density of etch pits has appeared too low. Studies via X-ray diffraction have been much more rewarding as to densities of imperfections, and, of course, yield a great deal more information.

Regarding (3): One run of growth in excess hydrogen was reported; a resonator of the crystal was made and examined at the Signal Corps, showing nothing remarkable. Growth in oxygen might be a method of increasing the number of non-bridging oxygen atoms in quartz and thus verifying, by lowered Q of the resonator at 50°K, the structure of the defect proposed by King (Ref. 23, p. 65).

Regarding (4): One experiment was made in the hope of producing screw dislocations in minor-r plates (Run 50G-4). On this orientation spiral mounds have been found and reported⁽⁸⁾ (28). AT-cut plates $3/4 \times 1 \frac{1}{4} \times 1/16$ in. (the $3/4$ in. being parallel to the X-axis) were cracked half way through the plate, along the projection of the Z-axis, by using a hot glass rod. Silver foil squares about 0.005 in. thick were held on opposite faces of the plate at the sides of the crack, and compressed across the plate thickness with small c-clamps thus providing a slight shear stress on the seed.

Two such units of plate and c-clamp were treated under the usual growing conditions for 2 weeks. The plates showed slight growth, gaining a total of about 5 g.

Examination at 36X discloses clear continuous growth over the cracks. The seed veil, assumed to be deposited at the onset of growth, could be easily examined below the grown minor-r face. The crack is always visible and dissolution obviously occurred into it from the original seed surface. The veil stops when the surface curves into the edge of the crack. The grown surface is flat over the crack over most of its length to the end, and near the most highly strained point the grown surfacing exhibits glossy depressions of irregular outline resembling areas of electrical twinning, i.e. areas which have become major-R, thus having a smaller growth rate.

Although quartz may be too brittle to be amenable to experiments performed on LiF and other crystals already subjected to such studies⁽²⁹⁾, a low bending stress should be sufficient to yield dislocations in new growth.

(28) Augustine, F., Hale, D., Phys. Chem. Solids, 13, 344-46 (1960).

(29) Gilman, J., Johnston, W., in "Dislocations and Mechanical Properties of Crystals," Wiley, 1957, pp. 116-163.

4.4.8 X-irradiation and Dichroism

An example of easily visible dichroism in aluminum-doped X-irradiated minor rhombohedral growth was observed in 1958. The specimen, uniformly colored, showed a variation in absorption color when held over a source of ordinary white light and oscillated about the projection of the c-axis. When the light was transmitted perpendicular to the c-axis, the use of a polaroid analyzer revealed that the transmitted e-ray is raspberry color and the transmitted o-ray is grayish green.

The specimen was prepared from a crystal grown in Run 54D-5; this and other Al-doped and Ge-doped crystals are further discussed in Ref. 8, p. 19 ff. The dichroism of smoky quartz and of irradiated synthetic quartz have been discussed by Cohen⁽³⁰⁾ who measured the optical absorption as a function of wave length for the e- and o-rays.

Dichroism has been observed particularly in the following specimens, all minor-r growth after irradiation:

Run 54D-5	(March 1958)	Al added to solution
Run 44C-22	(Nov 1959)	B " " "
Run 44B-8	(Jan 1958)	Ge " " "
Run B1 -5	(1954)	Normal process.

It is a question whether there are differences in the dichroism shown by plates darkened by X-rays, gamma-rays, or high voltage electrons. Visually there seem no distinction.

Spectrographic analysis shows that minor-r growth picks up more Al atoms than Z-growth, from a solution containing added aluminum, e.g. NaAlO_2 . Further, the aluminum in the r-growth is shown to be in a different situation, for it is shown to be related to the irradiation darkening exhibited by quartz, and greatly emphasized in r-growth doped with aluminum. The Al atoms in

(30) Cohen, A. J., J. Chem. Phys. Solids, 25, 908-14 (1956).

the r-growth (or probably any other darkenable growth) are in the sites ordinarily occupied by Si atoms, with a neighboring monovalent ion to compensate for the valence difference. The boron-doped quartz has not been examined as extensively as the aluminum-doped; minor-r growth darkens greatly compared to Z-growth, and it is supposed that observations and hypotheses applicable to aluminum would apply here.

An explanation of the darkening of minor-r quartz containing Al must cover the case of quartz containing Ge also, for both materials darken and show dichroism of visually the same hue. The latter material presumably contains Ge in Si sites, no balancing interstitials required, and also Al, although only half that in 54D-5.⁽³¹⁾

In the course of the project insufficient Al-doped Z-growth was produced to yield cuts parallel to the c-axis for examination of the dichroic effect under best conditions. Since Z-growth, even from solutions containing added Al, darkens almost inappreciably, such material may not be expected to show more than a mild effect. A Z-cut of Al-doped Z-growth, irradiated and viewed at an angle to the normal so as to get the effect of the absorption of the extraordinary ray did not yield visual evidence of dichroism.

It may be concluded with a fair degree of probability, that Al is not easily accepted in Z-growth in a position and orientation to yield dichroism, as happens readily in r-growth.

4.5 Summary of Materials Examined for Q

Quartz 43B-4:

Z-growth at low temperature and pressure in 20-liter vessel in run yielding several pounds of Y-bar growth. The growth rate was 0.14 mm/day, i.e. comparatively slow.

(31) Cohen, A. J., J. Chem. Phys. 28, 401 (1958).

Q at 100 Mc showed a uniform low level to -190°C ; the value for five resonators ranged between 37 and 55×10^3 .

Q at 5 Mc (precision resonator) varied from a high of 1.6×10^6 at room temperature to 5×10^5 at -190° with, however, two absorption peaks between, although no spurious resonances were found.

Chemical composition shows Al at 100, Fe high at 180, Na at 88 at impurity per million atoms silicon.

X-ray examination disclosed surprisingly uniform structure, with very little observable strain and only about 25 dislocation lines per cm^2 (Figs. 17 and 18). This result speaks well for slow growth under moderate conditions. Possibly if Al and Fe were better controlled the value of Q would be improved.

Quartz 54F-4:

Crystals mainly Z-growth, visually high quality, grown from Brazilian latices in 0.83 aqueous sodium carbonate at moderate temperature and pressure in a 2-liter vessel. A severe temperature drop at about 2/3 the total duration put a noticeable refractive index flaw in the growth occupying an approximate (0001) plane. The flaw resembles that of the joint in X-Z growth in a Y-bar, except it is much more visible.

Precision 5 Mc resonators showed Q at 70°C of 2.6×10^6 , average two units, measured by supplier. At about -190°C , Q dropped about 1.5 decades presumably moving toward the high loss 50°K point. One resonator in helium-filled envelope shows, on the contrary, a loss peak at -110°C , and below this, Q remains high (1.8×10^6). It is hypothesized that the refractive discontinuity may be involved.

On X-irradiation with about 6×10^6 r, no apparent darkening occurred.

Optical and X-ray photographs reveal the presence of a variety of dislocations with a density of about $10^2/\text{cm}^2$.

Chemical composition: Al low at 17; Na high at 130 atoms impurity per million atoms silicon.

Overall Conclusions: The presence of relatively large density of dislocations including a discontinuity visible as a refractive index change does not preclude obtaining a precision resonator of high Q.

Quartz SARP 4-17 and 4-23:

These two materials were grown at substantially the same conditions⁽³²⁾. They, and the other reported materials, SARP 5-38 and SARP 7-19, were grown from Brazilian nutrient, 0.83 molar sodium carbonate, degree of filling about 0.8, crystallizing temperature 355°C. The SARP 4-17 and 4-23 were grown on Z-cut seed.

Q for 5 Mc precision resonator from SARP 4-17 starts at 0.5×10^6 (av. 2 resonators, room temp.) and at -190°C is falling very rapidly. The resonator from SARP 4-23, made much earlier and supplied through the U. S. A. Electronics R & D Laboratory, is from high temperature electrolyzed material to judge from circumstantial evidence. (Cf. Ref. 32, Table IV Part C (p.52), and Fig. 14). It exhibits a Q of about 2×10^6 at room temperature, and a Q of 1.4×10^6 at -190°C, characteristic of the effect of high temperature electrolysis.

The available chemical composition data do not yield a clear picture. Comparing "SARP Typical Z" in Table III with data on 4-23 included in the Sawyer Research Products Report, the two aluminum contents are 33, and 22 to 66 atoms per million Si, and should be expected to be similar because of the similarity of growth conditions. Sodium content is also as expected, 52 and 26 to 78 atoms per million Si. However, the analysis "SARP Swept Z" made by Clevite on a quantitative basis with an accuracy of $\pm 10\%$, indicate a much larger percentage of iron and, more puzzling, a high sodium content. Electrolysis has been found to yield a sodium-containing deposit on the cathode⁽²³⁾. A decrease of Na content with electrolysis is also indicated by the infrared absorption studies of Kats (Ref. 16, (32) Sawyer, B. Contract DA-36-039-SC-81245, Final Report, January, 1961, p. 42,44.

p. 167). To resolve the questions raised by the analytical discrepancy, it would be desirable to compare data taken by the same organization. It is generally agreed that electrolysis between Pt electrodes removes sodium, and the removal of sodium ions (with substitution by hydrogen) has been considered an important factor in the improvement of Q.

Quartz from 4-17 was available for optical and X-ray examination. It showed a moderate dislocation density of 100 cm^{-2} to 400 cm^{-2} .

Quartz SARP 5-38:

The crystal was grown under moderate pressure and temperature, on a Y-bar seed, with temperature difference and growth rate higher than the other SARP materials. The composition of this quartz was determined by Clevite and agrees well with the "SARP TYPICAL" determined for Sawyer Research Products.

Q for this crystal from room temperature downward, begins at 1.1×10^6 and from -160°C drops rapidly to 10^5 .

The optical and X-ray views show a surprisingly low dislocation density, in contrast to what the higher growth rate might have suggested.

The material would be expected to show good Q behavior to low temperature after high temperature electrolysis.

Quartz SARP 7-19:

Conditions of growth similar to other SARP materials. The crystal was grown on a Y-bar seed, and in an unusually large vessel, 10" ID.

Q for this material behaves as for materials SARP 4-17 and 5-38: over a million at room temperature (1.3×10^6), and falling rapidly below -160°C .

Z-cuts from the crystal, examined optically and with X-rays, show distinctly the three growth types in the crystal, Z, X_f , X_g . Layered growth

of sharper and more diffuse detail are visible in the X_f and X_g materials respectively in the optical picture, and contrasting fine lines are visible extending into these materials from the Z-growth in the X-ray picture. X- and Z-growth in the Z-cut plate, examined with a petrographic microscope, show that the materials are biaxial, the angle being about 3° .

The optical view displays the Y-bar seed. Other texture is revealed in considerable amount. The effect of all this on the resonator quality may be small, since the blanks are cut from the crystal area presumably containing little, if any, X-growth.

Dislocation line density estimated at $100/\text{cm}^2$ in the Z, double this in the X-growth.

Overall conclusion: This Y-bar growth seems typical with respect to contrasting properties of Z- and X-growth. After electrolysis the low temperature Q would probably be much improved.

Quartz WE 16 March 1962:

This material from Western Electric Company, and identified by the date received, was grown rapidly at high pressure. The seed was a Z-cut, a Y-bar seed broad in the X-direction. The seed itself is riddled with liquid-vapor inclusions. The X-ray study indicates that the growth process may extend a dislocation from each liquid-vapor inclusion, and add others. The count was over 10^3 lines/ cm^2 .

Available spectrochemical data are normal and reasonably low, indicating that a growth rate of up to 20 times that shown by various Clevite crystals does not necessarily increase the contamination. Thus the quartz from Run 43B-4, grown at low temperature and pressure, contains a greater amount of aluminum and iron.

The material was not expected to show high Q. The value fluctuated between 0.2×10^6 and 0.5×10^6 through the temperature range studied.

5. CONCLUSIONS

5.1 Conclusions Relating to Q:

It has been commonly assumed for most kinds of crystals that their normally encountered dislocation content was of the order of a million lines per square centimeter. Little previous work has been done on quartz. Zimonyi⁽³³⁾ used etch pit counts to obtain suggested dislocation densities of 10^6 to $10^7/\text{cm}^2$. By very indirect calculation from their observed $20^\circ\text{K} - 5 \text{ Mc}$ "dislocation" peak of internal friction, Bömmel,⁽¹⁾ et al., obtained $850 \text{ lines}/\text{cm}^2$. VonKeymeulin⁽³⁴⁾ obtained some dislocation decoration in quartz after electrolyzing in silver; his pictures show the straight lines and a fountain-like array that is shown in several X-ray photographs in this report.

As a general rule, the quartz studied on the current contract contained less than $1000 \text{ dislocation lines}/\text{cm}^2$, with values ranging down to none/ cm^2 . Those with higher contents were, for the most part, crystals grown under anomalous conditions and/or exhibiting other rather obvious structural deformities.

It was hoped that such a wide variation in dislocation content might be shown to give rise to a correspondingly clear variation in internal friction, or Q, behavior. Both currently made measurements and those made on an earlier contract were compared with the pictorial evidence. An attempt is made in TABLE IV to summarize the results. It was not found to be possible to establish a clear and direct correlation between Q and dislocation content. There is some suggestion that the very highest dislocation densities are found in crystals of the poorest low temperature Q, at whatever frequency measured. None of the low temperature measurements were carried down far enough to show where the rising loss curves actually

(33) Zimonyi, G., Acta Physica, Acad. Sci. Hungaricae, 8, No. 1 and 2, 1957.
(34) VonKeymeulin, J., Naturw., 44, H18, p. 489, 1957.

TABLE IV

RUN	DISLOCATION DENSITY per cm ²		Q(5Mc) x10 ⁶		Q(100 Mc)	
	Z-growth	X-growth	Low Temp.	Room Temp.	Low Temp.	Room Temp.
Clevite 51 C-6	10 ³ to 10 ⁴	-	-	-	Poor	.074 x 10 ⁶
Clevite 54F-4	800	-	1 high 2 low	2 to 3	-	-
Clevite 43B-4	25	Fast 25 Slow 200	Fair	> 2	High	0.075 x 10 ⁶
Clevite 54B-5		1000 to 5000	-	-	Poor	0.040 x 10 ⁶
SARP 4-17	100 to 400	-	Poor	0.4 to 0.8	-	-
SARP 5-38	25	~	Poor	1.1	-	-
SARP 7-19	100	200	Poor	1.4	-	-
SARP 4-23	-	-	High	2	-	-
(Most prob- ably swept)						
WE(16 Mar. 1962).	> 1000	> 1000	Low	< 0.5	-	-
WE 23-13	~ 500	-	-	-	High	.057 x 10 ⁶

peak; thus it cannot be said whether the poorer low temperature Q curves are part of the Bömmel, et al.⁽¹⁾ 50°K - 5Mc "impurity" relaxation, or their 20°K-5 Mc "dislocation" relaxation, or else perhaps some other process that causes lesser humps in similar measurements. Some of the curves shown by Mason⁽³⁵⁾ have peaks in the general vicinity of 125°K; several of the curves in this report possess possibly nonspurious peaks in that approximate region. Krueger's high frequency measurements on a previous contract⁽²⁾ show numerous very small peaks.

The presence or absence of growth banding is another possible correlation with internal friction losses. As a periodic array, SARP 4-17 has them in the Z-growth, while Clevite 54F-4 does not; the Q of the former is rather poor while the latter is high. For other quartz studied the presence or absence of such banding cannot be positively ascertained without additional X-ray work. The presence of point-defect-induced halos in some of the Z-plate X-ray pictures suggests the presence of banded Z-growth; the areas of more steeply inclined topography of the growing surface can have directions of strain sufficiently inclined to the (10 $\bar{1}$ 0) or (11 $\bar{2}$ 0) diffraction planes as to be visible. Since most resonators are now made from Z-growth material, the presence of such banding must be looked for as "blankets" lying roughly along (0001) planes. As shown in a previous section, one must "see" these by diffraction from planes not perpendicular to (0001); unfortunately, most of the pictures were for practical reasons taken with (10 $\bar{1}$ 0) or (11 $\bar{2}$ 0) diffraction planes.

Since these growth bands are visible to X-rays and presumably contain varying concentrations of point defects, they must therefore represent a variation from one to another in density or elastic properties, or both. The "interfaces" between bands should act as very weak acoustic reflectors; energy

(35) Mason, W. P., Physical Acoustics and the Properties of Solids, Van Nostrand, Princeton, 1958, Chapt. X.

so reflected might be expected to be partially or completely lost by thermal dissipation, and therefore contribute to lowered Q. An attempt was made to deduce theoretically whether such considerations might be plausible:

One takes internal friction as

$$\frac{1}{Q} = \frac{\alpha V_s}{4.3f}$$

where α is the is the attenuation in db/cm of the acoustic wave amplitude A in passing through 1 centimeter of crystal, V_s is the shear velocity of the sound wave; and f is the frequency. If the internal friction in the SARP 4-17 resonator is $(0.5 \times 10^6)^{-1}$ and "good" quartz has a value of $(2.5 \times 10^6)^{-1}$, while $V_s = 3 \times 10^5$ cm/sec and $f = 5 \times 10^6$ sec⁻¹, then the increased attenuation in the poorer resonator is $\alpha = 1.15 \times 10^{-4}$ db/cm. One then takes the amplitude and acoustic impedance for incident, transmitted, and reflected waves at each "interface" respectively as A_1 , A_2 , A_3 , Z_1 , Z_2 , and Z_1 , following Brillouin's⁽³⁶⁾ notation. For an average growth band spacing d, the amplitude attenuation per interfacial reflection is given by

$$d\alpha = 20 \log_{10} \frac{A_1}{A_2} ,$$

or,

$$\frac{A_1}{A_2} = 1 + \frac{d\alpha}{8.7} .$$

For the SARP 4-17 resonator, it was observed that $d = 5 \times 10^{-3}$ cm;

(36) Brillouin, L., Wave Propagation in Periodic Structures, McGraw-Hill, 1946, p. 85 et seq.

as a consequence $A_1 \approx A_2$ and A_3 is negligibly small. If these considerations are applied to the energy conservation requirement that $A_1^2 Z_1 = A_2^2 Z_2 + A_3^2 Z_1$ and also to the relationship $Z = (c\rho)^{1/2}$ where c is the elastic shear modulus and ρ is the crystal density, we find that for this example

$$\frac{c_1 \rho_1}{c_2 \rho_2} \approx 1 - \frac{4d\alpha}{8.7} = 1 - 2.6 \times 10^{-7}.$$

Thus, with these assumptions, a variation in density and/or elasticity of a quarter of a part per million across opposing sides of each interface would account for the observed reduction in Q . In actuality, variations in either the quartz lattice constant (and therefore, possibly, density as well) or elastic modulus have been reported in the range of 10 to 100 parts per million for homogeneous crystals. It would certainly seem reasonable, therefore, to find variations in banded crystals of at least the order required by the above calculation. At the same time, this treatment assumes that all the energy of the small reflections is dissipation loss; it further treats the banding as if the density of point defects varied in a square wave fashion. It could well be that part of the reflected wave energy is coherent and therefore not lost; it further seems probable that the interfaces between bands are not sharply defined, and they may scatter acoustic waves more weakly.

This loss mechanism here speculatively advanced should be amenable to further analysis by the theories of scattering, rather than those for relaxation processes. As such, its first order effects should be independent of temperature, and might appear from experimentation to be a part of the losses previously ascribed to resonator mounting. A comparison of our measurements of Q vs temperature for SARP 4-17 resonators with those made from 54 F-4 show, indeed, that the former have the higher loss throughout the temperature range studied.

Among the runs yielding resonators of intermediate Q values, SARP 5-38 exhibits halos in the Z-growth, Z-plate X-ray pictures that are probably indicative of banding; SARP 7-19 appears to possess clear Z-growth, but possesses strongly banded X-growth. This latter observation may be significant, inasmuch as the X-growth in SARP 7-19 crystals comprises so much of their volume that it likely forms a part of the finished resonators.

If the point defects that constitute the bands have sufficient diffusivities, one should be able to alter this hypothetical banding scattering by annealing. Electrolytic "sweeping" would perhaps be found to be yielding some of its beneficial effects because of "smoothing"⁽²³⁾ the peaks and valleys of band composition. King shows that major changes in Q are effected by annealing and sweeping of what he calls Z" quartz, which is characterized by a high 130°C loss peak that worsens on annealing but is drastically reduced by sweeping. This quartz furthermore shows a "growth-banding" of light-scattering precipitates after annealing. In contrast, his Z' quartz, which does not have the 130°C peak, neither forms the precipitate bands nor shows more than slightly improved Q after sweeping. It would be most interesting to make X-ray diffraction extinction pictures of these quartz types before and after each stage of treatment. The intensity of banded strain pattern in each would be expected to have a relationship to the Q^{-1} measurements. One hesitates to expect a simple correlation, inasmuch as King's data do show a temperature dependence not anticipated by the proposed scattering mechanism. Only careful study could determine the relative effects on Q of defect average concentrations as compared to "banded" variations about the same mean value.

5.2 Other Conclusions Relating to Defects

1. The dislocations in quartz appear to vary in concentration from zero to perhaps $10^4/\text{cm}^2$.

2. These dislocations are very straight, and lie in direction approximating a 15° cone around the direction of growth.

3. Where the necessary X-ray comparison photographs were made, the dislocations appear to be edge type. This is not in conflict with the observation of growth spirals on the surface, inasmuch as any edge dislocation not perpendicular to a growing surface, must form a spiral component at the surface.

4. Dislocations are generated at discontinuities, such as seed surfaces, inclusions, or intense local gradients of point defect concentration.

5. The etch tubes produced in quartz by previous observers are formed along dislocations. The X-ray pictures that we made after such etching were too poor for reproduction here, but the lines are still visible. This suggests that the strain region around each dislocation line is not completely removed by the dissolution process.

6. Quartz can be locally biaxial, up to 3° observed for the 2V angle. As a measure of lattice strain, this could, in theory, be used to relate the acoustic impedance to other properties.

7. The polarized light technique is a simple and inexpensive means for assessing the general concentration of dislocations and degree of growth banding, being limited, however, to crystals in which these phenomena are roughly parallel to the Z-axis.

Conclusions related to crystal growth:

Extremely high purity quartz has been shown to be realizable, through control of nutrient, solution, and metal walls enclosing the system; and results obtained suggest that the purity can be pushed even higher -- a tentative figure would be another order of magnitude.

High freedom from dislocations has been effected, and although not consistently, the achievement proves that such quality can be had by attention to the parameters involved. It was shown by x-ray diffraction contrast that dis-

locations in grown material arise partly from pre-existing dislocations in the seed. Therefore, seed can be chosen such that with proper growth conditions, dislocation-free crystals can be grown.

Amorphous silica of selected purity can be made to yield crystals of high visual quality, the cause of crevicing having been traced to excess supersaturation, as was shown by running tandem experiments. Such excess should be controllable through the growing conditions, in particular temperature difference, pressure, and concentration of alkaline solution.

6. RECOMMENDATIONS FOR FUTURE WORK

A specific laboratory research project is recommended:

The addition of phosphorus to quartz structure as a compensating impurity against the documented damaging influence of aluminum impurity. If the expected effect is found, this step may be useful as a control means, overriding fluctuations in impurities such as aluminum.

In general it seems that the upper limit to the quality of synthetic quartz as regards Q has been reached for high frequencies because of an intrinsic loss mechanism of the structure, possibly to be explained by phonon viscosity. It was shown⁽²⁾ that at frequencies of 100 to 180 Mc the acoustic absorption as measured by Q approaches the limit found through a different technique by Lamb, et al.⁽³⁷⁾

Ultra high frequency transmission studies of BC-cut quartz have shown lower attenuation for this than for the AC-cut⁽³⁸⁾. A similar relation for the BT-cut compared to the AT-cut can be expected. The BT-cut should therefore be reconsidered for use in the 100 to 200 Mc range.

(37) Lamb, J., Redwood, M., Shteinshleifer, Z., Phys. Rev. Letters, 3, 28, (1959).

(38) Bömmel, Dransfeld, Phys. Rev., 117, 1245-52 (1960).

The best quartz grown by the "Signal Corps process" (as developed under contract by Brush-Clevite and commercially used by Sawyer Research Products) has Q within a factor 2 of the best natural quartz for the normal operation range (-80 to +80°C), and becomes equivalent to natural quartz when "swept".⁽³⁶⁾ The remaining problem is that of identifying and controlling the conditions giving the optimum crystals. It is therefore felt that the major burden of quartz improvement now rests with the manufacturers.

Further research on elastic wave dissipation through scattering by growth banding is recommended. This would best be carried out as part of a substantial continuing program on quartz texture as outlined below:

A. Dislocation defects in quartz need detailed classification. The rather skeletal evidence suggests that essentially only edge dislocations are present in quartz, and that they lie in certain preferred directions with certain preferred Burgers vectors. This picture needs verification; further, its relationship to the quartz atomic lattice and to the growth process needs to be determined. If it should ever be found that a special advantage can be ascribed to dislocation-free quartz, the observations made so far show that the crystal growing process could be improved to that end.

B. In previous research, the studies of irradiation darkening in quartz have been extremely valuable, demonstrating that point defects are not at all uniformly distributed. The time required for darkening is rather long and is destructive of the sample in the sense that it is altered from its original state to some irreversible degree. The use of X-ray diffraction (and optical) photography is a nondestructive and relatively rapid technique for showing many details of point defect distribution. It would be of interest to discover whether (1) all the "growth bands" described would be evidenced by irradiation darkening, and (2) all areas of irradiation darkening have associated lattice strain (previous to darkening) as to cause them to appear as "growth bands" in X-ray diffraction or polarized light photographs. In the one or two examples studied, where some such comparison could

be made, the answer to both questions is "yes, but not exactly."

C. There is a host of other things not known about growth banding and other nonuniform distributions of point defects, for example, their chemical nature, and, indeed, whether or not some of them are simply lattice vacancies induced, perhaps, by a critically high degree of supersaturation during growth. It may be that they all constitute concentrations of sodium and aluminum that can be precipitated as light-scattering silicate aggregates by King's⁽²³⁾ annealing process. In the case of Z-growth banding, it should be determined by X-ray diffraction photography to what degree the strain within growth bands is altered by either annealing or electrolytic sweeping. The infrared absorption work of Laves⁽¹⁷⁾ and others indicates that regions of higher concentration of hydrogen in quartz correspond to those of (a) irradiation darkening, (b) strain, evidenced by polarized light, (c) precipitated "blue haze", perhaps similar in composition to King's⁽²³⁾ silicate aggregates, and (d) lower Q. Microanalytical techniques would be needed, together with mass spectrometry, to obtain impurity content of more precision than the oft times ambiguous ultraviolet spectroscopy.

If the phenomena of "growth-bands" are due to variations in growth supersaturation, the number and intensity of these alterations in lattice composition should correspond to some common measure of growing conditions, for example variation of autoclave temperature. At the same time, such comparisons must be made with a knowledge of the impurity concentrations in the growing solution. Thus, the banding may require both temperature variation and certain impurities. Naturally, it is assumed that the impurity content of the growing solution stays reasonably constant during a run, and does not change rapidly because of pockets of impurities in the lasca nutrient being gradually dissolved.

D. Finally, Q measurements made in conjunction with these proposed growth and defect studies should be extended down to liquid helium temperatures and up to at least 200°C. This must be done to determine which of the dislocations, growth bands, infrared absorptions, and measured impurities correspond to the reported internal friction relaxation peaks. If part of the Q loss in banded quartz is due to the hypothesized scattering mechanism, it should appear as being independent, or nearly so, of temperature. Wherever possible, the actual resonators used in Q measurements should be directly examined by X-ray diffraction photography, by infrared absorption, and by microchemical analysis.

Respecting one of the above items, impurities, Fraser⁽³⁹⁾ has inserted ions of Li, Na, and K into natural quartz by means of high temperature electrolysis, and has observed the increased acoustic absorption at the respective temperatures, 100°K, 50°K, 200°K.

These univalent ions can remain in the quartz presumably only by attaching themselves to sites occupied by trivalent substitutional ions. Hence the identification of these peaks with three elements confirms that the growing of high purity material should yield material showing no peaks of acoustic absorption in the lower temperature range, i.e. quartz of improved quality. This aspect of quality, however, is aside from the observation, made in this Report, that resonators from quartz of high dislocation density may yet exhibit high Q over much of the range from room temperature to -190°C. Furthermore, higher purity may lower the dislocation density still further, through offering fewer strain points from which dislocations could start (Run 50J-1, p.54).

Pfenninger⁽⁴⁰⁾ showed that quartz can be infiltrated by metal ions such as Au, Ag, Cu. The effectiveness of such technique in studying resonator plates is well demonstrated.

(39) Fraser, D.B., Bull. Am. Phys. Soc., Program Washington Meeting, 22 April, 1963 (Vol. 8, p. 354).

(40) Pfenniger, H., Thesis, "Diffusion of cations and Precipitation of Metals in Quartz by means of an Electric Field," University of Zürich, 1961.

7. IDENTIFICATION OF PERSONNEL

The following key personnel contributed to the program as indicated during the period January 1, 1962 through December 31, 1962:

Danforth R. Hale	-	Project Scientist	-	1023 hrs
Allan E. Carlson	-	Project Chemist	-	1027 "
Helmut H. A. Krueger	-	Physicist	-	177 "
William A. Gilroy	-	Technician	-	1236 "
Others			-	744 "
TOTAL				4207 "

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